

Explanation of the Material Anomalies of Water (M1-M14)

- ✓ No aqueous solution is ideal
- ✓ D₂O and T₂O differ significantly from H₂O in their physical properties
- ✓ Liquid H₂O and D₂O differ significantly in their phase behavior
- ✓ H₂O and D₂O ices differ significantly in their quantum behavior
- ✓ The mean kinetic energy of water's hydrogen atoms increases at low temperature
- ✓ Solutes have varying effects on properties such as density and viscosity
- ✓ The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise
- ✓ The dielectric constant of water is high
- ✓ The dielectric constant shows a temperature maximum
- ✓ Proton and hydroxide ion mobilities are anomalously fast in an electric field
- ✓ The electrical conductivity of water rises to a maximum at about 230 °C
- ✓ Acidity constants of weak acids show temperature minima
- ✓ X-ray diffraction shows an unusually detailed structure
- ✓ Under high pressure water molecules move further away from each other with increasing pressure

M1 No aqueous solution is ideal

Ideality depends on the structure of the solvent being unaffected by the solute. Water is not even close to being a homogeneous phase at 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 H₂O do not behave ideally.^j Although most non-aqueous solutions also show deviations from ideality at higher concentrations, the deviations that occur in aqueous solutions are generally much more extensive. [

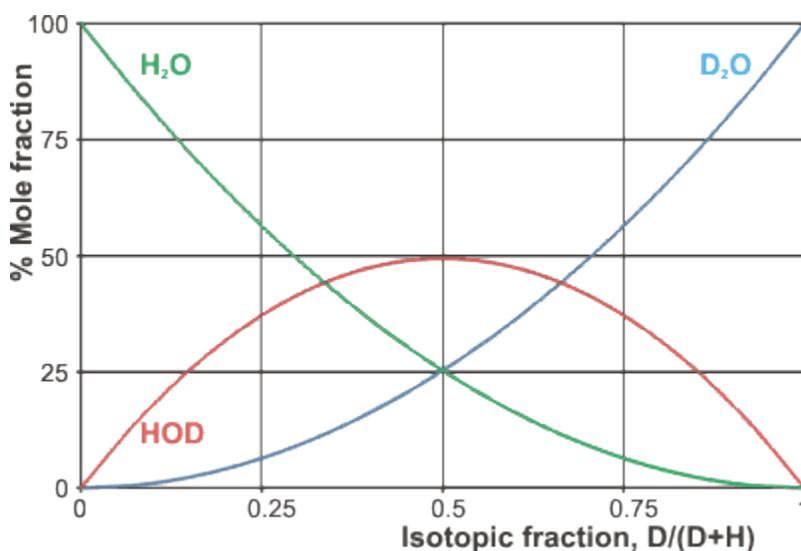
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M2 D₂O and T₂O differ significantly from H₂O in their physical properties

Normally different isotopic forms of compounds behave very similarly to each other. However, nuclear quantum effects in the water molecule are significant and differ between the isotopic forms. The heavier forms of water (D₂O where D = deuterium, 2.0141 g mol⁻¹; and T₂O where T = tritium, 3.0160 g mol⁻¹) form stronger hydrogen bonds than light water (H₂O where H = protium, 1.0078 g mol⁻¹) and vibrate less. Hence, they are more ordered than normal water, as shown by their greater molar volumes, are more tetrahedral and have more hydrogen bonds [1485]. This causes many of their properties (such as the viscosity, self-diffusion coefficient, protein solubility, toxicity^a and effect on the frequency of circadian oscillations [1395]) to be different from those expected from a simple consideration of their increased mass (for example, the D₂O/H₂O viscosity ratio rises from about 1.16 at 100 °C to around 2.0 in deeply supercooled water [23b]). This difference appears as a shift in the equilibrium position equivalent to a slight increase in temperature [425]; for example, viscosity data has been reconciled if the temperatures are shifted by 6.498 °C and 8.766 °C for D₂O and T₂O respectively [73].^b H₂O is about four-fold stronger as an acid than D₂O at 25 °C and H₃O⁺ in H₂O is 1.5 times as strong an acid as D₃O⁺ in D₂O. Remarkably, the difference in the specific heat minimum between H₂O and D₂O is over 80 °C. Most of the differences between the behavior of H₂O and D₂O may be explained as due to the nuclear quantum effectsⁱ inherent in the large mass difference between the hydrogen and oxygen atoms [554]. Although the electron densities of the different isotopic forms of liquid water have proved, so far, to be indistinguishable [566], it is expected that the O-D bond length is shorter than that of O-H due to its smaller asymmetric vibration and the smaller Bohr radius of D relative to H. This gives rise to

small differences in the size and direction of the dipole moment between HDO and H₂O [1174], which further confuses any analysis of the structure of water containing mixed hydrogen isotopes.

Almost pure H₂O and D₂O exist^m but HDO can never be more than about 50% pure, existing only in the presence of both H₂O and D₂O. Mixtures of H₂O and D₂O equilibrate (via proton transfer by self-dissociation and recombination) to form HDO:



which is close to a total randomization of the hydrogen atoms (that is, equal concentrations of HOH, HOD, DOH and DOD that would be $K_{\text{eq}} = 4$) but is reflected in a slight preference for the partitioning of the deuterium-containing species into the more extensive and stronger hydrogen-bonded clusters.¹ ΔH is the enthalpy of mixing. Thus a mixture of 20% D₂O and 80% H₂O (by volume and by mol; ~11 mol D₂O per liter solution) gives a mixture of 64% H₂O, 32% HDO and 4% D₂O (by mol, ~36 M H₂O, ~2 M D₂O and ~18 M HDO). The K_{eq} decreases with decreased temperature [126a] and increased hydrogen bond cooperativity [985]. Even the properties of HDO deviate from those expected from a consideration of the properties of H₂O and D₂O [126b], with the D-atom preferring to be hydrogen bonded over the H-atom except where the H-bond is particularly short (as in H₅O₂⁺) [985]. Surprisingly, D₂O does not mix as readily with H₂O as might be pre-supposed [1472], presumably as the preferred D₂O clustering holds the D₂O molecules together. This tendency gives rise to anomalous cooling curves in unstirred D₂O/H₂O mixtures [1472], slow equilibration and unexpected entropic effects [1855]. Mixing 1:1 H₂O and D₂O gives rise to a small heat of mixing (~1.3 kJ mol⁻¹).

The vibrational spectrum of HDO is fundamentally different from either H₂O or D₂O due to the separation of the two hydroxyl (O-H and O-D) vibrations in HDO but their combined motion in H₂O and D₂O. In HDO the H atom is more reactive and more easily dissociated than the D atom. As hydrogen bonding is a property of at least two water molecules, isotopic mixtures contain many differently paired (and more extensive) species each of which may present different properties to those in natural liquid water. It is clear that care must be taken over extrapolating the properties of H₂O/D₂O mixtures (often used in neutron scattering and vibrational spectroscopic studies) to those of normal liquid water (that is, 99.97% H₂O). For example, D₂O is preferentially found at hydrophilic interfaces [1342].

Liquid T2O is corrosive due to self-radiolysis (${}^3_1\text{T} \rightarrow {}^3_2\text{He}^+ e^- + \bar{\nu}_e$). The β particles travel only about 6 μm in water and even dilute solutions of HTO produce gaseous hydrogen (including HT) and redox-active products including highly reactive hydroxyl radicals ($\cdot\text{OH}$ and $\cdot\text{OT}$).

Even H218O behaves differently from H216O due to reduced quantum translational motions, reducing the size of the first shell local hydrogen-bonded tetrahedron but leaving the non-bonded water distances almost the same [1035]. Although D₂O has similar mass (only 0.04% heavier than H₂¹⁸O), its behavior much more affected by the isotopic substitution, due to the altered mass distribution influencing its librations and hence the local environment of both the first and second aqueous shells [1035]. H₂¹⁷O and HDO behave as different molecules to H₂¹⁶O in mixtures with H₂¹⁶O as shown by their colligative properties, the freezing points rising with the molality of H₂¹⁷O or HDO (freezing points rising here as they form mixed solid solutions) [1470]. [[◀ Anomalies page : Back to Top ▲](#)]

M3 Liquid H₂O and D₂O differ significantly in their phase behavior.

The phase behavior of liquid H₂O and D₂O differ, with the triple point of D₂O being 3.82 °C and 49 Pa higher than that of H₂O, their vapor pressure curves crossing at 221 °C and the critical point of D₂O being 3.25 °C and 393 kPa lower [1007]. This isotope effect has its origins in the reduced zero point vibration of D₂O that reduces its van der Waals volume (by about 1%) and its associated repulsive effect within the hydrogen bonds at lower temperatures, so increasing the D₂O-D₂O hydrogen bond strength.^c At higher temperatures the transition to the excited state is more easily accomplished in D₂O ($\sim 2450\text{ cm}^{-1}$, relative to H₂O $\sim 3280\text{ cm}^{-1}$). Due to the asymmetry of the vibration, this increases D₂O's effective van der Waals volume and reverses the relative repulsive effect, so reducing the D₂O-D₂O hydrogen bond strength at higher temperatures.^d

The miscibility properties of liquid H₂O and D₂O also differ, with 3-methylpyridine being always miscible in liquid H₂O but immiscible in liquid D₂O between 38.5 °C and 117 °C at normal pressure [1976]. [[◀ Anomalies page : Back to Top ▲](#)]

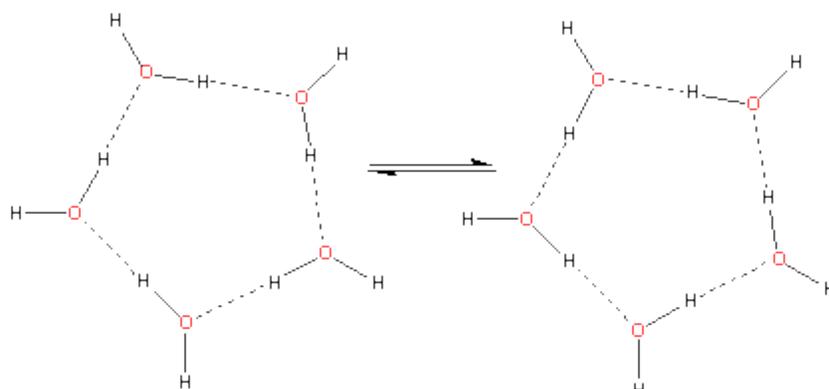
M4 H₂O and D₂O ices differ significantly in their quantum behavior.

Replacing hydrogen (¹H) by deuterium (²H) results in a greater volume ($\sim 0.1\%$) of hexagonal ice. This is in contrast to the expected behavior (e.g. solid ²⁰Ne is 0.6% more voluminous than ²²Ne) due to the expected greater nuclear motion of lighter isotopes [1819]. Furthermore, the anomalous effect in water increases with temperature, even though a normal isotope shift should decrease with temperature [1819]. This anomalous behavior is due to the significantly greater covalent O-H asymmetric vibration.

As the K_{eq} decreases with decreased temperature [126a] and increased hydrogen bond cooperativity [985] (see above), at temperatures close to 0 K this may mean that H₂O and D₂O may form separate phases and are no longer in equilibrium [985]. [[◀ Anomalies page : Back to Top ▲](#)]

M5 The mean kinetic energy of water's hydrogen atoms increases at low temperature

The mean kinetic energy of liquid water's hydrogen atoms reaches a maximum at about 7 °C then reduces on cooling to a minimum value at about 0 °C.^k However at supercooled temperatures below this, the proton mean kinetic energy increases substantially [1596]. This indicates that, under supercooling, the hydrogen bonded donor protons in liquid water clusters undergo coherent transfer to their acceptor hydrogen bond partner water molecules, such as:



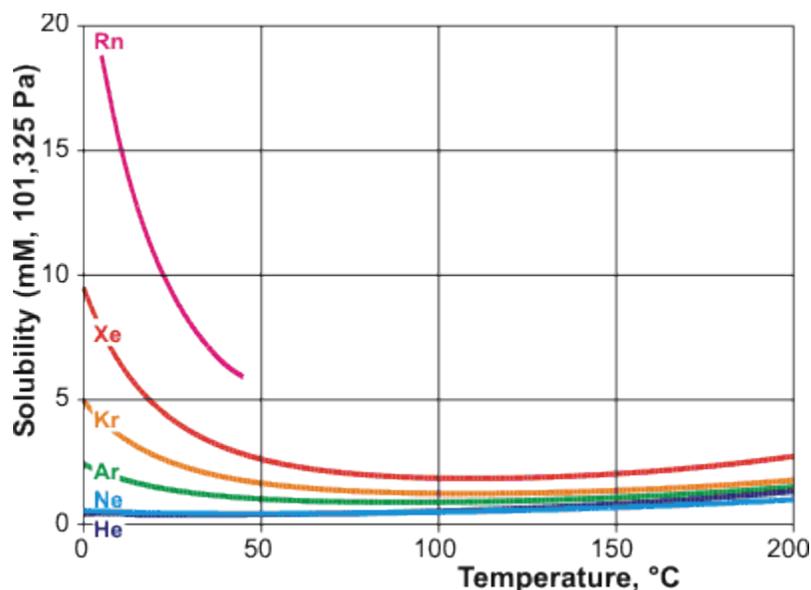
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M6 Solutes have varying effects on properties such as density and viscosity

Solute will interfere with the cluster equilibrium by favoring either open or collapsed structures. Any effect will cause the physical properties of the solution, such as density or viscosity, to change. Solute have a lower than expected effect on both the cryoscopic (that is, effect of solute on freezing point depression, $1.86 \text{ K kg mol}^{-1}$, compare CCl_4 30 K kg mol^{-1}) and ebullioscopic constants due to water's low molar mass and high heats of fusion and evaporation respectively. [< Anomalies page : Back to Top >]

M7 The solubilities of non-polar gases in water decrease with increasing temperature to a minimum and then rise.^e

Non-polar gases are poorly soluble in water. Most gaseous solutes dissolve more in most solvents as the temperature is raised. However, non-polar gasses are much more soluble in water at low temperatures than would be expected from their solubility behavior at high temperatures.



The solubilities of the noble gases are shown opposite [IAPWS, 1166] and given below. Their hydration may be considered as the sum of two processes: (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 dispersion interactions (for example, krypton dissolved in water is surrounded by a clathrate cage with $20 \text{ Kr} \cdots \text{OH}_2$ such interactions [1357]). In water at low

temperatures, the energy required by process (A) is very small as such pockets may be easily formed within the water clustering (by CS \rightarrow ES)^f.

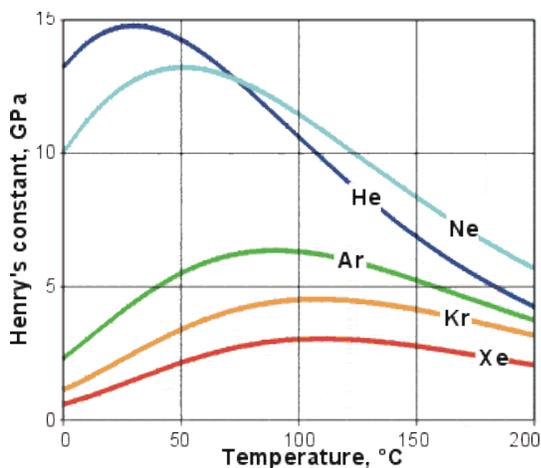
Using the noble gases to investigate the solvation of non-polar gases is useful as they are spherically symmetrical and have low polarizability, whereas shape and polarizability may confuse the hydration of other gases. The solubility of the noble gases increases considerably as the temperature is lowered. Their enthalpy and entropy of hydration become more negative as their fit into the water dodecahedral clathrate improves.

Solubility properties of the noble gasses							
Property		He	Ne	Ar	Kr	Xe	Rn
Atomic number		2	10	18	36	54	86
Atomic radius, Å [1167]		1.08	1.21	1.64	1.78	1.96	2.11
ΔG° of solution in H ₂ O at 25 °C, kJ mol ⁻¹ [1296]		29.41	29.03	26.25	24.80	23.42	
ΔH° of solution in H ₂ O at 25 °C, kJ mol ⁻¹ [1296]		-0.59	-3.80	-11.98	-15.29	-18.99	
ΔS° of solution in H ₂ O at 25 °C, J mol ⁻¹ K ⁻¹ [1296]		-100.6	-110.1	-128.2	-134.5	-142.2	
Solubility, mM, 5 °C, 101,325 Pa [1166]	H ₂ O	0.41	0.53	2.11	4.20	8.21	18.83
	D ₂ O	0.49	0.61	2.38	4.61	8.91	20.41
Solubility minima, °C [IAPWS, 678]	H ₂ O	30	50	90	108	110	
	D ₂ O	53	53	98	108	116	

Oxygen (O₂) and nitrogen (N₂) molecules behave similarly (solubility minima of N₂ at 74 °C and O₂ at 94 °C, IAPWS), although their solubilities are low (O₂, 1.92 mM in H₂O, 2.14 mM in D₂O; N₂, 0.94 in H₂O, 1.05 mM in D₂O; all at 5 °C, 101,325 Pa [1168]).

The greater solubility of O₂ over N₂, in spite of its lesser clathrate forming ability [1168] has been proposed due to its formation of weak hydrogen bonds to water [1168].⁹

The solubilization process is therefore exothermic (that is, has negative ΔH) and (as predicted by Le Chatelier's principle) solubility decreases with temperature rise. At high temperatures (often requiring high pressure) the 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 (being fully miscible under supercritical conditions).



The more attractive the solute-water van der Waals dispersion interactions (due both to atomic number dependency and goodness of fit within the clathrate pocket), the greater the inherent exothermic nature of the process and therefore the higher the temperature minimum (see Table above) and the greater the temperature range of negative temperature solubility coefficient. Similarly Henry's constants (= partial pressure/mole fraction;^hrepresents volatility, see opposite) exhibit increasing maxima with increasing size (the maxima are the same as the solubility minima above).

The poor solubility of non-polar gases in water, in spite of the negative enthalpy change on dissolution, is due to positive free energy change (+ve ΔG) attributed to the anomalously large negative entropy change (-ve $T\Delta S$) caused by the structural enhancement of the water (ES) clusters; a conclusion reinforced by the enhanced heat capacity of these solutions (+ve C_p , characteristic of a decrease in the degrees of freedom of the water solvent). This structural enhancement may include the fixing of the cluster centers, preventing the randomizing flickering between clusters otherwise evident, as well as ordering the inner dodecahedral water shells surrounding the solute molecules. There is also a reduction in volume (-ve ΔV) showing a reduction in the unoccupied space within the water solvent and also indicative of the gases occupying the pre-existing, if collapsed, clathrate sites.

Counter-intuitively in spite of it forming stronger hydrogen bonds, D_2O is a better solvent than H_2O for non-polar gases, as it is a more static molecule and more easily forms the ES water clustering. Therefore D_2O can accommodate the guest molecules more easily without breaking its hydrogen bonds [874]. Addition of positively hydrating salts (for example, LiCl) that destroy the water low-density ES clustering reduce the solubility ('salt out') of the non-polar gases whereas hydrophobic hydrating salts (for example, tetramethylammonium chloride) that increase water low-density ES clustering stability also increase non-polar gas solubility ('salt in'). Small 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 with respect to their diameters has a maximum (and their free energy of hydration has a minimum) when diameters are about the same as that of the dodecahedral cavities (that is, $\sim 4.5 \text{ \AA}$) in the icosahedral network [196]. The solubility behavior of larger hydrophobic molecules is discussed briefly elsewhere. It should also be noted that the solvent properties of liquid superheated water also change with temperature as water's dielectric permittivity reduces towards that of common organic solvents as the temperature rises towards its critical point.

Even though the amount of air (that is, $N_2 + O_2 + Ar$) dissolved in water is very low, it is sufficient to lower the density of water by almost 5 ppm (that is, 0.0005%) at 0 °C [870].

It should be clear from the above discussion that the solubility of non-polar gases (at equilibrium), in water at its boiling point, is not zero; an error propagated by some text-books. The non-equilibrium production of steam would, however, lead to the temporary loss of dissolved gas from the liquid phase but this would increase the pressure in the closed system required for solubility determinations.

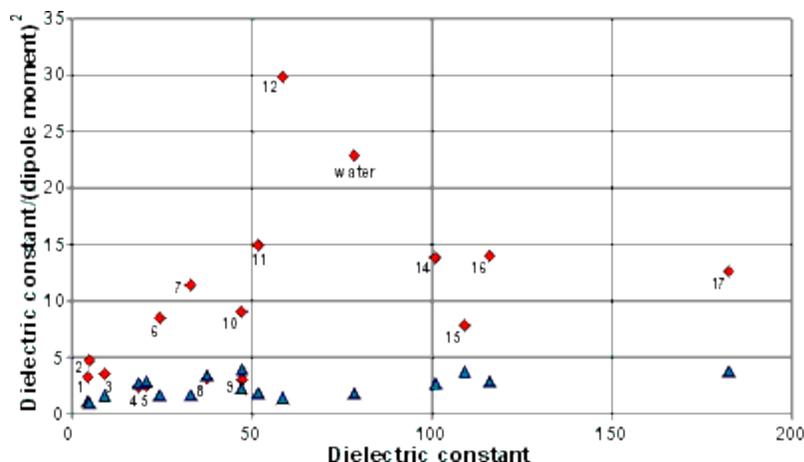
The solubility of gases (and other solutes such as salts) in ice is very low. This explains the usefulness of freeze-thaw operations under reduced pressure for degassing water. [ Anomalies page : Back to Top 

M8 The dielectric constant of water is high (78.4 at 25 °C)

The high dielectric constant of water and its small molecular size both combine to endow water with the strong ability to dissolve salts. Polar molecules, where the centers of positive and negative charge are separated, possess dipole moment. This means that in an applied electric field, polar molecules tend to align themselves with the field. Although water 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 (permittivity). Because water possesses a hydrogen bonded network that transmits polarity shifts extensively through rapid and linked collective changes in the orientation of its hydrogen bonds, it has a high dielectric constant. This allows it to act as a solvent for ionic compounds, where the attractive electric field between the oppositely charged ions is reduced by about 80-fold, allowing thermal motion to separate the ions into solution. On cooling, as the water network strengthens and water's dipole moment increases, the dielectric of liquid water climbs to 87.9 (0 °C), increasing on conversion to ice then increasing further as the ice is cooled. An *ab initio* molecular dynamics study showed that the increase of the average dipole moment (due to hydrogen bonding) of water molecules and the local alignment of these molecular dipoles both contribute almost equally to this high dielectric constant [1672].

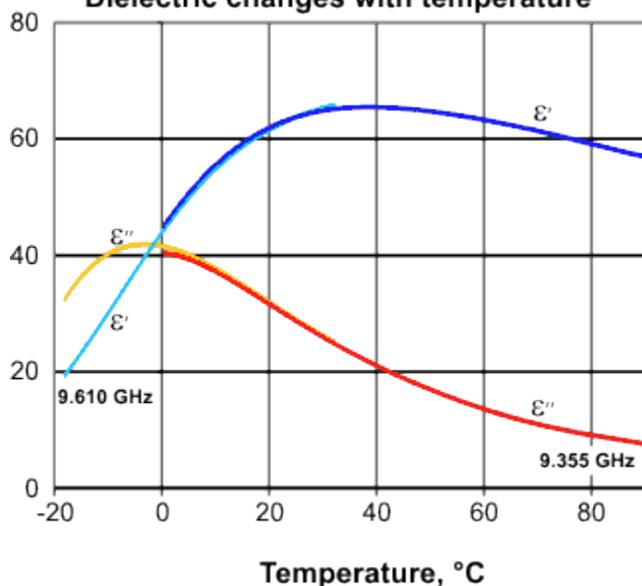
On heating, the dielectric constant drops, and liquid water becomes far less polar, down to a value of about 6 at the critical point. The dielectric constant similarly reduces if the hydrogen bonding is broken by other means such as strong electric fields but not with pressure. The change in dielectric with temperature gives rise to considerable and anomalous changes in its solubilization and partition properties with temperature, which are particularly noticeable in superheated water [610] where the dielectric is low, and in supercooled water where the dielectric is high and increases (107.7 at -35 °C, with a sudden jump to >10,000 at -40 °C in nano-sized pores [1774]) even as the density decreases. Pressure increases the dielectric constant (101.42 at 0 °C and 500 MPa), due to its effect on the density.

Perhaps the high dielectric constant of water should not be considered anomalous as other small polar molecules (with higher dipole moments) form liquids also having high dielectric constants (see below). The ratio dielectric constant/(dipole moment)² is often also reckoned, by others, to be anomalously high in liquid water (but note that the gas-phase, rather than liquid, dipole moments are used for comparing these substances). Although high, clearly molecules with zero dipole moment (*e.g.* CCl₄) have infinite such values. Also anomalous is the 60% increase in the static dipole moment of water molecules in liquid water when compared with the gaseous state. This is due to the effect of hydrogen bonding causing greater intermolecular charge transfers during the changed distance between the molecular charge centers. Interestingly, the dynamical dipole momentⁿ is not similarly enhanced, and may even be reduced, due to the electrostatic dragging effect of surrounding electrons [1993].



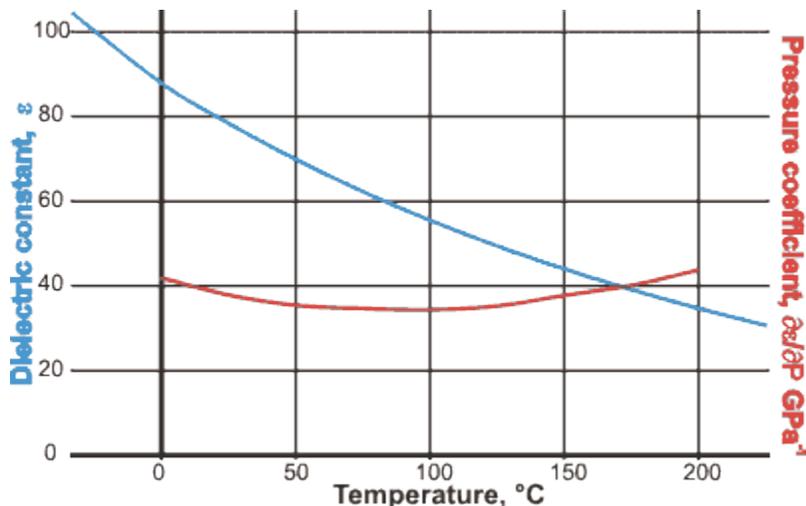
Shown opposite are the dipole moments (blue triangles below) and dielectric constant/(dipole moment)² ratios (red diamonds above) relative to the dielectric constants for a range of solvents. The data 1-17 correspond to 1, diethyl ether; 2, chloroform; 3, methylene dichloride; 4, methyl ethyl ketone; 5, acetone; 6, ethanol; 7, methanol; 8, acetonitrile; 9, ethylene glycol; 10, dimethyl sulfoxide; 11, hydrazine; 12, formic acid; 13, water; 14, sulfuric acid; 15, formamide; 16, hydrogen cyanide; and 17, N-methyl formamide respectively. [[◀ Anomalies page : Back to Top ▶](#)]

M9 The relative permittivity shows a temperature maximum. Dielectric changes with temperature



Anomalous dielectric behavior of water is found over a range of microwave frequencies between about 2 and 100 GHz whereby the real (ϵ') and/or the imaginary (ϵ'') part of the complex dielectric constant increase then decrease with increasing temperature. Examples at two close frequencies for liquid (including supercooled) water are shown opposite [588]. This may be understood by noting the shifts with temperature of the maximum frequency of microwave absorption and the dielectric permittivity. Analysis of the complex permittivity gives a discontinuity at about 30 °C [1045].

There is a frequency (2.96 ± 0.17 kHz.) where the relative permittivity (strictly speaking, the dielectric constant is the relative permittivity of a material for a frequency of zero) is independent of temperature (the isopermittive point). Below this frequency the relative permittivity increases with temperature, above, it decreases. This has been explained by considering water as a system of two species: ions and dipoles [1698].



The dielectric constant increases considerably at low temperatures but it is the change in this with pressure that shows an unusual behavior [1912] with a minimum at about 95 °C due to the two-state structuring of liquid water.

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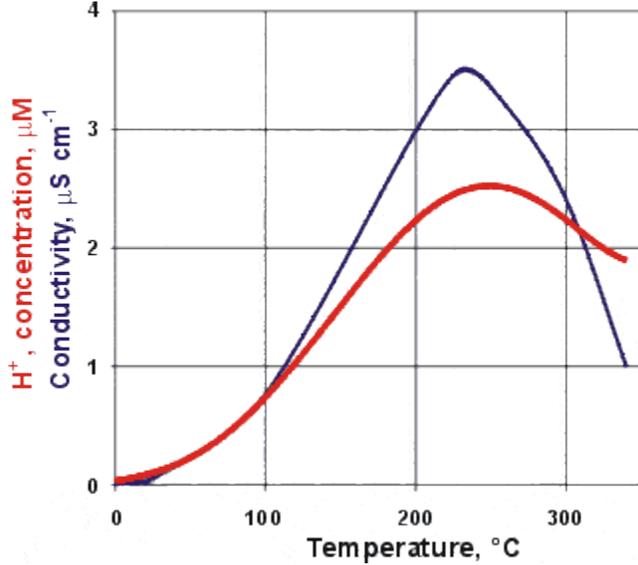
M10 Proton and hydroxide ion mobilities are anomalously fast in an electric field.

The ionic mobilities of hydrogen ions and hydroxide ions at 361.9 and 206.5 ($\text{nm s}^{-1}/(\text{V m}^{-1})$) at 25 °C are very high compared with values for other small ions such as lithium ($40.1 (\text{nm s}^{-1})/(\text{V m}^{-1})$) and fluoride ($57.0 (\text{nm s}^{-1})/(\text{V m}^{-1})$) ions. This is explained by the Grotthuss mechanism.

The limiting ionic conductivities are related (= mobility x charge x Faraday) and their values for hydrogen ions and hydroxide ions, at 349.19 and 199.24 $\text{S cm}^2 \text{mol}^{-1}$ at 25 °C [737], are similarly very high compared with values for other small ions such as lithium ($38.7 \text{S cm}^2 \text{mol}^{-1}$) and fluoride ($55.4 \text{S cm}^2 \text{mol}^{-1}$) ions.

Another anomaly that may be related is the preliminary report of an increase in both anion and cation mobilities at pH between 2.5 and 4.5 [1442]. [< Anomalies page : Back to Top >]

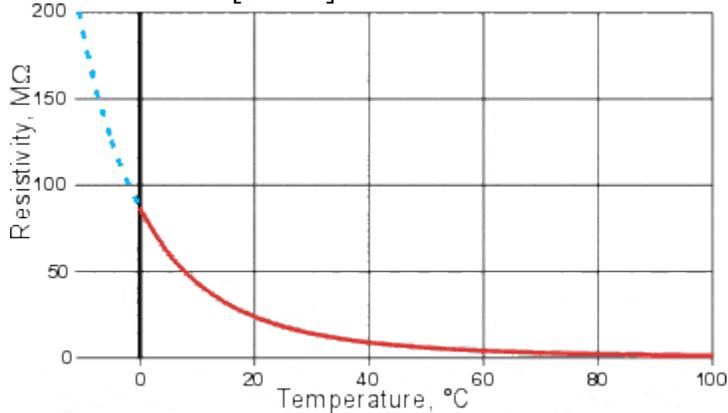
M11 The electrical conductivity of water rises to a maximum at about 230 °C and then falls.



The electrical conductivity of water increases with temperature up to about 230 °C due mainly to its increased dissociation producing higher concentrations of the highly conducting H⁺ and OH⁻ ions, which reach maximum concentrations at about 249 °C [IAPWS].

Above this temperature, for liquid water in equilibrium with the vapor, the density is much reduced (for example, 0.7 g cm⁻³ at 300 °C) and this reduces the ability for dissociation. Proton mobility decreases above 149 °C due to lowered amounts of 'Zundel' cations (that is, H₅O₂⁺) [1061].

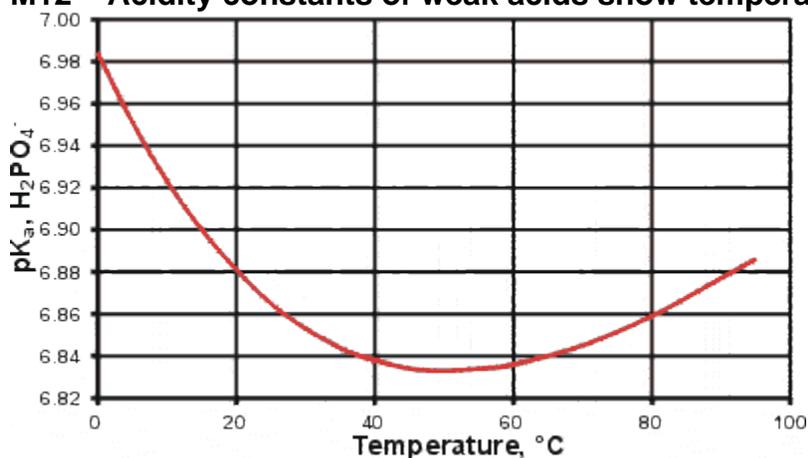
Note that the pK_w also reaches a maximum value at about 249 °C in line with that of the hydrogen ion concentration [IAPWS].



Opposite is shown the great increase in the resistivity (= 1/conductivity) of water at low temperatures [737]; extrapolated values are shown in dashed blue. Interestingly, the electrical conductivity of water increases on degassing [711]. Together these properties support the formation of ES clusters at low temperatures and in the presence of non-polar gases, which involve localized and limited isotropic hydrogen bonding and so prevent lengthy directed proton movements.

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M12 Acidity constants of weak acids show temperature minima.



An interesting anomaly concerns the changes in the pK_a with temperature of many weak acids. As an example, opposite is shown this for the second dissociation of phosphoric acid;



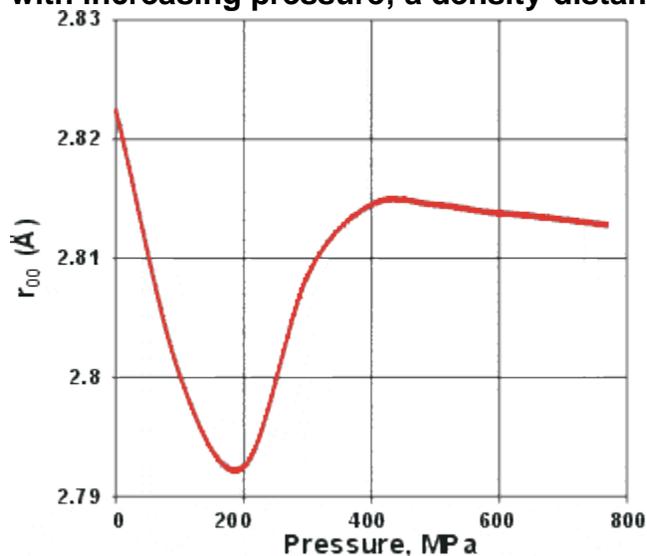
Such changes are due to a combination of factors including changes in the dielectric (high temperatures increasing the pK_a) and hydrogen bonding (low temperatures increasing the pK_a). [

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M13 X-ray diffraction shows an unusually detailed structure

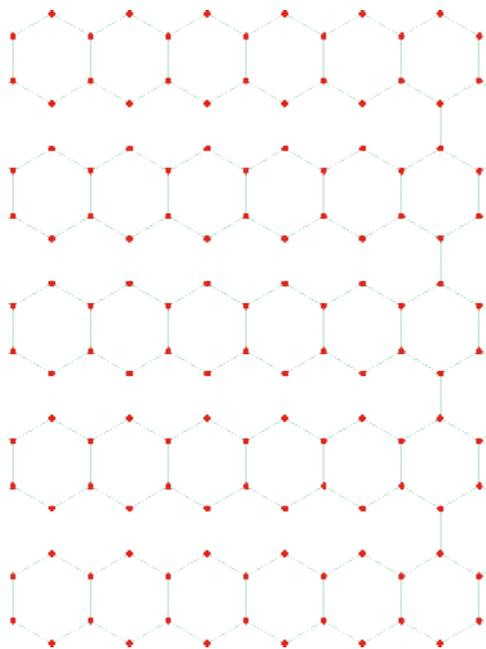
This is shown elsewhere and is simply explained by the presence of ordered clustering within the liquid phase. [◀ Anomalies page : Back to Top ▶]

M14 Under high pressure water molecules move further away from each other with increasing pressure; a density-distance paradox.



When liquid water is put under pressure (below about 200 MPa) the water molecules approach their neighbors more closely, as might be expected from the increase in density. However, if the pressure is increased from about 200 to 400 MPa, the average distance between neighboring water molecules increases [51]. At higher pressures the distances reduce again (but less so) with increasing

pressure. A similar and corroborative behavior is seen with the O-H stretch vibration frequency (ν_1), which increases with pressure between about 200 to 400 MPa [533] whilst reducing with pressure at higher or lower pressures. The O-H stretch data has been confirmed at 23 °C but not found at 52 °C, indicating that it requires larger clusters to be recognized [824]



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 (see cartoon left where interpenetration increases the density without reducing the intermolecular distances. Such behavior can also be seen to cause other anomalies (1, 2, 3, 4, 5). When liquid water is put under pressure (below about 200 MPa) the water molecules approach their neighbors more closely, as might be expected from the increase in density. The interpenetration of the water networks gives rise to a high density water of similar character to the interpenetrating high density ices. The 200 MPa pressure required for the formation of this high density water has also been confirmed by infrared spectroscopy [2099]. The bond lengths in the tetrahedral glass GeO_2 also behaves similarly as they increase under increasing pressure from 5 GPa to ~ 30 GPa when the coordination of the Ge atoms increases [1930].

A similar effect is found in supercooled water where the distance between the water molecules decreases [1489] as the density decreases as the supercooling temperature is lowered, the decrease in density being primarily due to the reduction in nearest neighbors. Also similar is what happens in the high density ices where, for example, ice-seven (with two interpenetrating cubic ice lattices) under a pressure of over 2200 MPa (density 1.65 g cm^{-3}) has an average $\text{O}\cdots\text{O}$ nearest neighbor distance about 3.5% greater than that in cubic ice (density 0.92 g cm^{-3} at 0.1 MPa). Thus the density of ice-seven is somewhat less than twice the density of cubic ice (that is, $2 \times 0.92 / (1.035)^3 = 1.65 \text{ g cm}^{-3}$). Also, neighboring water molecules in hexagonal ice lie closer than those in liquid water but the ice density is less, due to ice molecules having only four neighbors. [[Anomalies page](#) : [Back to Top](#) ▲]

Footnotes

^a D₂O is toxic to many organisms at high levels (20%-100% D₂O, where it affects many processes including mitosis and membrane function) but is not generally considered harmful at much lower levels where it is used in human physiological research. It would take many days of drinking 2-3 liters a day of deuterated water for a person to be poisoned enough to die. There is some evidence to show that artificially reducing its natural abundance in water (0.03% w/w) may have positive effects on the health of organisms [424]. [Back]

^b This method for reconciling the data works poorly at low temperatures [1049]. [Back]

^c The reduced zero point energy when switching D-atoms for H-atoms from free to hydrogen bonded positions within water clusters has been shown due to the energetic consequences of the lowering of the bend and torsional bond energies which are greater than the raising of the stretching bond energy [986]. [Back]

^d Also contributing to this effect are the relative isotopic differences between the zero point energies of the liquid and gaseous phases. Librational vibrations (due to hydrogen bonding) release energy when the phase changes from liquid to gaseous (where they are absent) with H₂O librations (being greater) releasing more energy and so increasing the volatility of H₂O relative to D₂O at lower temperatures. Opposite effects are apparent at higher temperatures where there is less hydrogen bonding but energy still needs to be supplied to provide for the increased zero point vibrational energy of the stretch vibrations (the gaseous stretch vibrations being more energetic than those for the liquid phase) [992]. [Back]

^e In many gaseous-solute solvent systems (for example, N₂ in CCl₄), the solubility increases with temperature increase. Although solubility decreases with temperature increase is encountered with some other solute-solvent combinations (for example, methane in *n*-heptane), the behavior is a more general property of water and deserves comment. [Back]

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

^g The formation of O=O···H-OH hydrogen bonds may be seen as the first stage in the natural low-level formation of oxygen redox products (for example, H₂O₂) in water. As the ratio of O₂/N₂ solubilities has a maximum at 290 K, there is indication that partial clathrate cages may be responsible for the polarization that encourages the hydrogen bond formation. [Back]

^h Henry's constant = partial pressure/mole fraction (K_H) may be described by the following

$$K_H = \frac{p}{X} = \frac{RT}{V_{H_2O}} e^{\left(\frac{\mu}{RT}\right)}$$

equation . where p is the partial pressure of the solute in the gas, X is the solute mole fraction, R is the gas constant, T is the absolute temperature, V_{H₂O} is the molar volume of water and μ is the temperature-dependent excess chemical potential of hydration for the solute [1276]. [Back]

ⁱ Nuclear quantum effects concern the different energies of the vibrational states. The bonds involving the deuterium atom (being about twice as heavy as the protium atom) vibrate with less amplitude and frequency. Nuclear quantum effects are seen particularly in differences in their zero point energy; the vibrational energy that remains at close to absolute zero. [Back]

^j The term 'ideal' indicates adherence to a particular equation; it does not indicate any more basic truth. [Back]

^k It should be noted that a simulation does not show this anomaly [1760]. [Back]

^l Within LDA clusters the equilibrium lies more to the left with HOD molecules being somewhat excluded [1779]. [Back]

^m D₂O is highly hygroscopic, absorbing water vapor from the atmosphere and so decreasing in D₂O and increasing in HDO, if handled in open vessels. [Back]

ⁿ The dynamical dipole is the behavior of the dipole (μ) upon molecular rotation, $\partial\mu/\partial\Omega_\xi$ ($\xi = x, y, z$), where Ω_ξ is the molecular rotation coordinate around the ξ axis [1993]. [Back]

Source:<http://www1.lsbu.ac.uk/water/explan3.html>