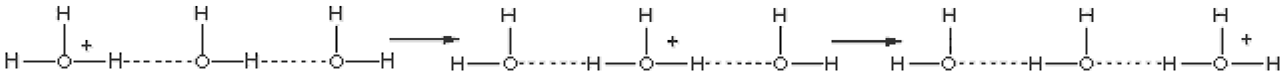
Grotthuss mechanism

- **Diffusion of hydrogen ions**
- **Diffusion of hydroxyl ions**
- **The ionic product, K_w**
- **pH**
- **Hydrogen ions**
- **Hydroxide ions**

It is generally thought that protons and hydroxide ions rapidly diffuse in liquid water [102], with protons diffusing almost twice as fast as hydroxide ions (and seven times as fast as Na^+ ions). However, it should be recognized that these diffusivities are determined from movement in an electric field (at 100 v m^{-1} ; H^+ and OH^- have mobilities of 36.23 and 20.64 μm s^{-1} respectively at 298 K)[a], where the special mechanisms described below are operational, and the true diffusive movements of the ions may be somewhat less (particularly as they are attached to their attendant hydrogen-bonded water and accompanied by thier counter ions), as can be recognized by the proton diffusional limitations that take place at the surface of some immobilized enzymes [103].

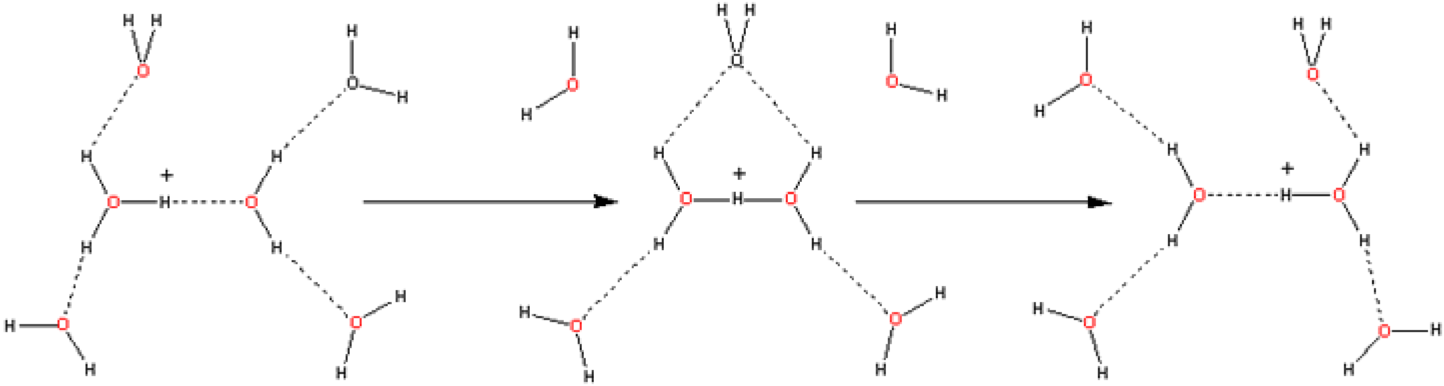
Diffusion of hydrogen ions

The Grotthuss mechanism (origin in [160]), whereby protons tunnel from one water molecule to the next[b] via hydrogen bonding, is the usual mechanism given for facilitated proton mobility (see also an alternative mechanism below). The process is similar to that of autodissociation; the mechanism causing the ions (H^+, OH^-) to initially separate. Both processes increase with increasing temperature [1041].



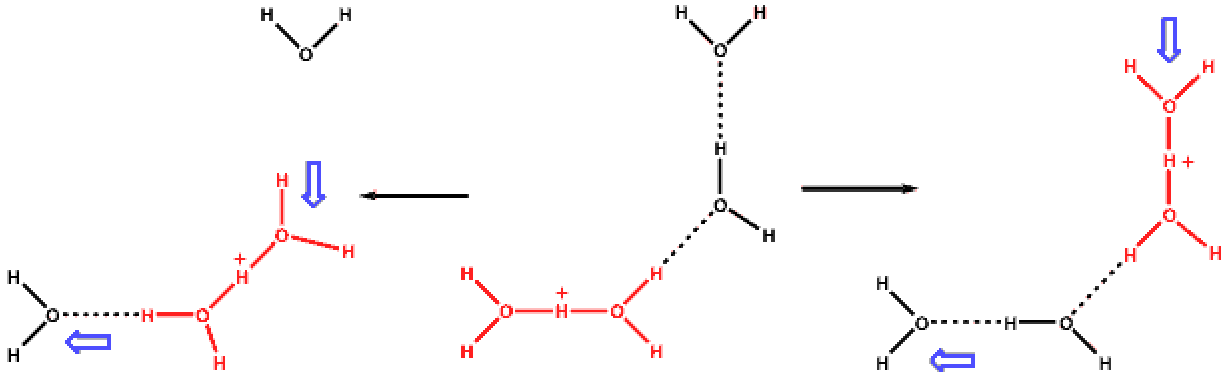
It is noteworthy that this process, although faster than translational diffusion, proves to be much slower than might be expected from its mechanism. This relative sluggishness may be due to the rotation of molecules required for trains of sequential proton movement (see below) and the consequential necessity for the breakage of hydrogen bonds. The strange effect of degassing increasing proton diffusion over ten-fold, however, indicates that the non-polar dissolved gas molecules, naturally present, disrupt the linear chains of water molecules necessary for the Grotthuss mechanism and so slow the proton movement [711]. Over short hydrogen- bonded water wires there can be correlated movement of protons due to quantum fluctuations [2025] and extremely rapid transit through the existing suitably hydrogen bonded water wires [2026]. However, after a proton has moved along a chain of water molecules (in effect if not in body, by the excess proton disappearing at one end and appearing at the other end), it is clear that further proton movement requires a reorientation of the hydrogen bonding, if continued proton tunneling through the same molecules and in the same direction is to proceed.

In order to migrate, the ions must be associated with hydrogen bonded clusters; the stronger and more extensive the cluster, the faster the migration. Stronger hydrogen bonding causes the O···O distance to be shorter, so easing the close approach required for transfer. A limiting factor in the mobility for both ions is the breakage of an outer shell hydrogen bonds. This enables the proton to transfer from H_3O^+ [102] and involves the additional energy requirements of stretching the outer hydrogen bonds due to the contraction of the O···O distance.



Oxonium ion transport mechanism

The triangular arrangement of water molecules [1488] formed during proton transfer, has also been found in the protonated trimer ($H_7O_3^+$, [138]), and necessarily involves a rotation around the hydrogen bond as the 'Zundel' dihydronium ($H_5O_2^+$) ion flattens from its normal tetrahedral structure. The presence of the fourth water molecule associated with the $H_9O_4^+$ cluster (shown above the charge above) is seen in a neutron diffraction study as oriented but distant (3.2 Å, [697]). Proton transport may also occur using 'Zundel' dihydronium ($H_5O_2^+$) ions only, as below [490], which involves the concerted movement of two molecules. Such proton jumps may be short (shown on left) or long (shown on right). An ab initio simulation [1061] favored this mechanism, where $H_5O_2^+$ mobility was induced by thermal movement in the second solvation shell. An external electrical field was found to ease the process by suitably orienting the water in this direction [1061]. It has been suggested that proton mobility above 149 °C decreases due to the decreasing amounts of $H_5O_2^+$ present [1061].

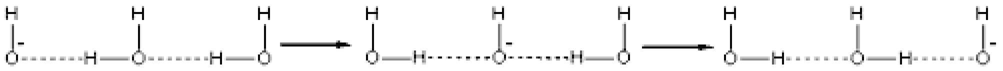


An additional and alternative mechanism has been proposed, using *ab initio* simulations but in agreement with the Zundel' dihydronium ($H_5O_2^+$) ions concentrations, by which the rapid diffusion of hydrogen ions, at temperatures below about 400 °C, is due to the high diffusion of these $H_5O_2^+$ ions, allowed by the weaker surrounding hydrogen-bonded water network [1117], (see also ionic kosmotropes).

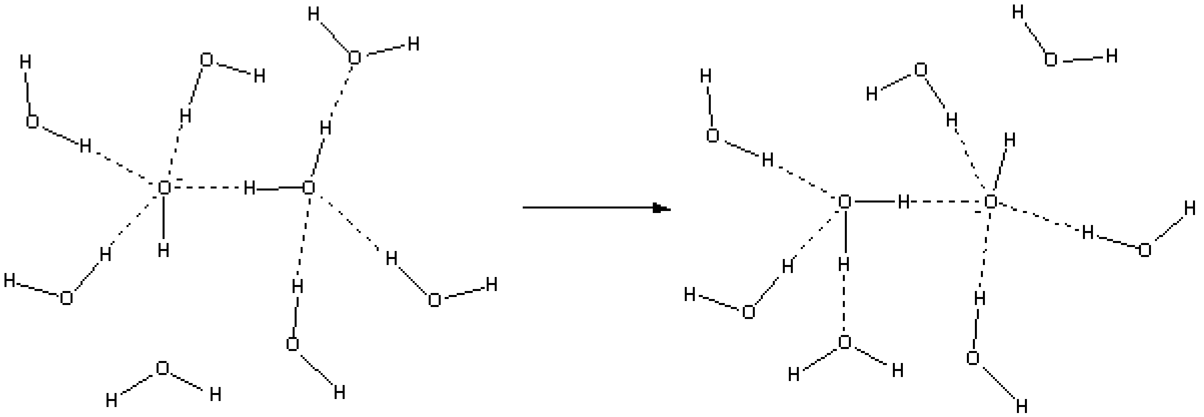
Proton transport in water, protein channels and bioenergetic proteins has recently been reviewed [1092]. It is interesting that aquaporin water channels deliberately re-orient water molecules to preclude sequential hydrogen bonding so preventing proton transfer by the Grotthuss mechanism.

Diffusion of hydroxyl ions

A similar process to that for hydrogen ions was initially proposed for hydroxide mobility:



However it is now thought that hydroxide ions make use of an entirely different mechanism [371] for diffusion in an electric field. It has been proposed that the movement of the hydroxyl ion is accompanied by a hyper-coordinating (that is, a fourth hydrogen bond donor) water molecule. The hydrated hydroxide ion is coordinated to four electron-accepting water molecules such that when an incoming electron-donating hydrogen bond forms (necessitating the breakage of one of the original hydrogen bonds) a fully tetrahedrally coordinated water molecule may be easily formed by the hydrogen ion transfer. The structure below left, $HO^-(\cdot\cdot HOH)_4$, together with the more distant oriented water molecule below it, has been seen using neutron diffraction, with empirical structure refinement, of concentrated NaOH solutions [698]. The different mechanism, involving extra hydrogen bond rearrangements plus re-orientations, is the reason for the reduced mobility of the hydroxide ion compared with the oxonium ion. Interestingly, the transfer involves an anionic trimer ($H_5O_3^-$), whereas hydrogen ion movement involved the cationic trimer ($H_7O_3^+$) (note that neither of these trimers are stable by themselves).



Hydroxide ion transport mechanism

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Footnotes

[a] Degassing may increase these values [711]. The data given is from Atkins' Physical Chemistry, 7th Ed. [Back]

[b] A similar hopping mechanism occurs with I^- in liquid iodine and Br^- in liquid bromine. [Back]

Source:http://www1.lsbu.ac.uk/water/grotthuss.html