

WATER IONIZATION

General: Although ions make up a very small proportion of the water mixture, they are significant all out of proportion to their numbers¹. Water is self-ionizing because of the strongly polar nature of the water molecule. Water ionizes spontaneously, although the extent of self-ionization is normally quite tiny². This means that ions are most likely to be separated by large numbers of un-ionized molecules under normal conditions.

In the free atmosphere water can also be ionized by hard radiation (especially *gamma* radiation), by friction, by electrostatic fields and discharges, and by a variety of other phenomena. Raindrops and cloud droplets are ionized by their simple passage through the air. A large portion of the atmosphere (the ionosphere) is strongly ionized, but all of it is ionized to some extent. This extent is not negligible.

Ionization Mechanism: The strongly polar nature of the water molecule encourages self-ionization. There are two protons (hydrogen nuclei) at one end that are attracted to any electrons in the vicinity. There are two pairs of electrons on the other end that are attracted to any protons in the vicinity. Attractions both stretch and bend the bonds—both hydrogen and covalent.

Both the internal movements of thermal agitation (libration and vibration) and the external movements (libration, vibration, and rotation) can stretch, bend, and break both intermolecular and intramolecular bonds. We have stated that the phase and density of water at any given time and place is the result of conflicts between forces of attraction and forces of repulsion. These forces are not static,

¹ In this essay and in “Water Structures” and “Water Clusters”, I am indebted to the superb series of summaries prepared and posted online by Martin Chaplin of the London South Bank University. No other source proved so useful or so cogent. See <http://www.lsbu.ac.uk/water/index2.html>

² At common atmospheric temperatures, the ratio of hydronium ions to un-ionized molecules is some 2.8×10^{-9} to one. Measurements of pH actually measure the concentration of the hydronium ion (H_3O^+), not the concentration of the hydrogen ion (H^+).

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but are dynamic in the extreme. Both common sense and mathematics tell us that bonds—even covalent bonds—are going to get broken. When they do, ionization is a common result.

Ionic Variations: All of the structures that we looked at in [Water Structures](#) are capable of forming ions and do form ions. The common dimer (H_4O_2) readily disassociates into one hydronium ion (H_3O^+) and one hydroxide ion (OH^-). The common quadramer (H_8O_4) disassociates into one Zundel cation (H_5O_2^+) and one anion (H_3O_2^-). All four of these ions are relatively stable, and persist for relatively long periods of time.

Other common ions include: H_7O_3^+ , H_9O_4^+ (the Eigen cation), $\text{H}_{13}\text{O}_6^+$, $\text{H}_{15}\text{O}_7^+$ (the icing ion), $\text{H}_{21}\text{O}_{10}^+$, and H_7O_4^- . Note that cations are readily produced by the addition of a captured proton to one of the water structures (protonation), while anions are readily produced either by the loss of a proton or by the addition of the hydroxide ion to one of the water structures (hydration). Finally, it should be noted that free electrons move about in abundance in the atmosphere, in liquid water, and in ice.

Although elementary treatments may refer to the ionization of H_2O into the hydrogen cation H^+ and the hydroxide anion OH^- , this almost never takes place for reasons having to do with quantum thermodynamics. In any case, the longevity of a naked proton in either water or ice would be measured in microseconds or less. This does not stop proton diffusion, of course; it simply means that the proton must “hop” or “tunnel” from molecule to molecule.

The Perfidious Proton: It should be emphasized that the hydrogen ion is both extremely fickle and extremely mobile in both water and ice. In the water molecule, each hydrogen ion (proton) changes its oxygen partner some thousand times or more each second. This rate, however, is far less frequent than the forming and breaking of that hydrogen ion’s hydrogen bonds with other molecules. It would appear that the hydrogen ion simply does not like to be “tied down”.

This “looseness” also extends to protonated ions. In water, the hydronium ion (H_3O^+) is far more mobile than the hydroxide ion (OH^-).

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Ionization and Structures: Ionization encourages the formation of multi-molecular structures and clusters, since the electrostatic force of the ionization potential is added to the electrostatic element of the hydrogen bond. The hydrogen bonds formed between ions and un-ionized water molecules are often twice as strong as those between un-ionized molecules. These bonding forces are not saturated, but extend well past simple neighboring molecules. It has been said that a simple hydronium ion can exert an influential force on more than a hundred surrounding water molecules. [111]

Summary: Ionization enhances the attractive intermolecular forces. Thus, a strongly ionized water droplet will attract ionized vapor molecules and structures having an opposite charge; whereas an un-ionized droplet would not exert that same attractive force. This increases the rate of forced influx. The addition of hygroscopic solutes and suspensions to the droplet, will serve to increase this forced influx even further.

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TABLE WIO01

SOME WATER IONS

ION	FORMULA	COMMENTS
Free electron	e^-	Abundant in all three phases of water: vapor, liquid water, and ice.
Hydrogen cation	H^+	Virtually never found unassociated as a “naked” proton. Extremely mobile, switching oxygen partners a thousand or more times a second.
Hydroxide anion	OH^-	Common disassociation product of water dimer (H_4O_2) and other water structures. Relatively stable.
Hydronium cation	H_3O^+	Common disassociation product of water dimer (H_4O_2) and other water structures. Relatively stable. Can donate three hydrogen bonds but accepts almost none.
Dimer anion	$H_3O_2^-$	Disassociation product, with the Zundel cation, of the common quadramer. Relatively stable.
Zundel cation	$H_5O_2^+$	Disassociation product, with the dimer anion, of the common quadramer. Relatively stable.
Eigen cation	$H_9O_4^+$	Consists of a hydronium ion strongly hydrogen-bonded to three water molecules ($H_3O^+(H_2O)_3$).
Icing ion	$H_{15}O_7^+$	Abundance increases as water temperatures approach freezing point. Usually structured as $H_3O^+(H_2O)_6$. Very stable.

REFERENCES

INTERNAL REFERENCES: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

[35] [Water Structures](#) – This is a more detailed discussion of water structures and molecular clusters. Topics include: how structures are non-polymeric, hydrogen bonding, bonding limitations and longevity, the basic nature of water structures, structures in water vapor, structures in ice, structures in liquid water, and the nature of surface tension.

CITATIONS: These are outside publications that are either specifically cited in this paper or whose content is significantly incorporated into this paper.

[108] Martin Chapin: **Hydrogen Bonding in Water**; retrieved 07/22/2008
<http://www.lsbu.ac.uk/water/hbond.html>

[111] Martin Chapin: **Water Ionization**; retrieved 07/21/2008
<http://www.lsbu.ac.uk/water/ionis.html>

[130] Department of Chemistry, Purdue University: **Intermolecular Forces**; retrieved 03/03/2008.
<http://chemed.chem.purdue.edu/genchem/topicreview/bp/intermol/in...>

[131] University of Waterloo: **Intermolecular Forces**; retrieved 03/03/2008.
<http://www.science.uwaterloo.ca/~cchieh/cact/c123/intermol.html>

GENERAL REFERENCES: These are works by other authors that contain general treatments of kinetic gas theory, statistical mechanics and thermodynamics, atmospheric physics, and other scientific fields that are used in the current paper. They primarily contribute conceptual frameworks; but offer specific scientific data on occasion.

[1016] D. Tabor; **Gases, Liquids, and Solids**; Third Edition; Cambridge University Press, 1991.