Liquid Water Structure

In liquid water, most of the water molecules have the same local environment as in ice but the long range structure of ice disappears due to motion of the molecules. Bonds between water molecules break and reform very rapidly and the individual water molecules are free to move through the substance. The structure of liquid water, with excess electron density at the oxygen atom and polar O-H bonds is responsible for its chemical properties.

Outline

- Bonding and Dynamics
- Water Interactions
- Self Ionization of Water
- Homework

Bonding and Dynamics

Hydrogen bonding

The ability of hydrogen atoms bonded to nitrogen, oxygen, or fluorine to bridge to other nitrogen, oxygen, or fluorine atoms is called hydrogen bonding. This interaction is important in the structure of water and a key to water's ability to solvate ionic substances.

Here is an animation that shows 10 water molecules interacting with one another and forming a water droplet. The molecules are oriented so that the hydrogen atoms are shared between two adjacent oxygen atoms.

from Eric Martz, proteinexplorer.org
**Gas-phase Water**

We’ve already talked about water in the gas phase. Water vapor consists of individual molecules of H\textsubscript{2}O.

We know from the molecular orbital diagram of water that there are 2 orbitals that are non-bonding or nearly non-bonding. In the structure at the right, the lines indicate electron density from these orbitals.

There is excess electron density around the oxygen atom and the hydrogen atoms have a partial positive charge. There should be strong intermolecular interactions but, in the gas phase, the high kinetic energy of the molecules prevents condensation.

Overall, there is no ordering to the molecules of gas phase water.

**Ice**

Let's move from the least ordered from to the most ordered. Solid water is ice.

This has an ordered packing in solution that consists of a diamond lattice of oxygen atoms bridged to the other oxygens by hydrogen. Each oxygen is bonded to 4 hydrogen atoms in a tetrahedron.

**Liquid Water**

But despite its prevalence and importance, liquid water is not as well understood in the other phases.

In the recent study, Nilsson and colleagues probed the structure of liquid water using X-ray Emission Spectroscopy and X-ray Absorption Spectroscopy. These techniques use X-rays, generated by a synchrotron light source, to excite electrons within a water molecule's single oxygen atom. Tuning the X-rays to a specific range of energies can reveal with precision the location and arrangement of the water molecules.

The researchers found that water is mostly made up of tetrahedral groups, as in ice, but there is also a less defined structure that seems to be like a distorted, hydrogen-bonded form of water vapor.
The oxygen atoms in distorted water molecules have 2 strong bonds to hydrogen and 2 weak ones. The oxygens in tetrahedral, ice-like water have 4 equivalent bonds to hydrogen.

Even in its tetrahedral form, liquid water is different from ice because the bonds are constantly breaking, the molecules of water moving, and more bonds forming.

Water is more dense than ice because of water molecules held within holes of the cubic close packed lattice.

Hydrogen Bonding, Lewis Acids and Lewis Bases

Hydrogen Bonds
In pure water, hydrogen atoms bridge between oxygen atoms to link individual water molecules into a 3-dimensional structure.

Hydrogen atoms of water can also bridge to nitrogen atoms, oxygen atoms, or fluorine atoms in other molecules when those atoms have a non-bonding electron pair. A hydrogen atom bonded to a nitrogen, oxygen, or fluorine atom in another molecule can bridge to the oxygen atom in water.
The hydrogen bonding interaction is the reason why molecules with OH groups, such as sugars, are so soluble in water.

Glucose, $\text{C}_6\text{O}_6\text{H}_{12}$, is at right.

**Donor-Acceptor Bonds**

We've previously only considered simple covalent bonds where each atom contributes 1 electron and 1 orbital. There is another type of bond where 1 atom contributes an empty orbital and the other contributes an orbital with 2 electrons. This is called a donor-acceptor bond.
Boron can only form 3 covalent bonds because it has only 3 valence orbitals. Molecules like BH3 are electron deficient, with only 6 electrons around the boron. Boron can combine its empty 2p orbital with the filled 2sp³ orbital on nitrogen to form a donor acceptor bond.

There are two ways to represent this. Even though it was formed by the combination of a filled and an empty orbital, the product can be represented as a covalently bonded molecule. In this representation there must be a positive formal charge on nitrogen and a negative charge on boron.

Another way of representing it is with an arrow from the nitrogen to the boron, showing that there is an overlap of orbitals but not a formal electron transfer.

Any molecule with a non-bonding electron pair that can donate its electron pair to form a donor-acceptor bond is called a Lewis base. An electron deficient molecule that can accept an electron pair from a Lewis base is called a Lewis acid. Many Lewis acids are metals or metal-containing molecules.

**Water as a Lewis Base**

Water is a Lewis base. When a salt such as NaCl dissolves in water, the sodium cation is solvated by water. The interaction between Na⁺ and H₂O is that of a Lewis acid-Lewis base complex. The Na⁺ is a Lewis acid and forms 6 donor-acceptor bonds with water molecules.

![Solvation of Na⁺ by water](image)

The water molecules around the sodium cation also form hydrogen bonds with other water molecules (not shown).

**Self Ionization of Water**

**Ionization Equilibrium**

The bonds between water molecules rapidly break and re-form. Sometimes the bonds break in an uneven way to give solvated H₃O⁺ and solvated HO⁻.
We typically abbreviate the cation part as $\text{H}^+(\text{aq})$ and the anion part as $\text{HO}^-(\text{aq})$ with the realization that the solvated proton and solvated hydroxide anion are complexes and stabilized by many water molecules.

Relative to water molecules, the concentration of $\text{H}^+(\text{aq})$ and of $\text{HO}^-(\text{aq})$ are very low, but because they are in equilibrium with liquid water, the concentrations are constant.

**pH and Acids**

Because of the self ionization, water is a Bronsted acid. That is, it produces $\text{H}^+(\text{aq})$ ions in solution. We can calculate the molar concentration of solvated protons from the expression for $K_w$. In neutral water the concentration of $\text{H}^+(\text{aq})$ and of $\text{HO}^-(\text{aq})$ must be equal.
We can define a quantity related to acid concentration, pH. The pH is -1 time the log of the hydrogen ion concentration. The pH of neutral water is 7.

\[
\text{H}_2\text{O}(l) \quad \rightarrow \quad \text{H}^+(aq) + \text{HO}^-(aq)
\]

\[\text{[H}^+(aq)] = 10^{-7} \text{ M}\]

\[\text{pH} = -\log(10^{-7}) = 7\]

We can determine the pH of any solution by converting the concentration to a power of 10. The pH is then -1 time the exponent. Remember that we've used an abbreviated log table to convert whole numbers to powers of 10.

**pOH and Bases**

Water is also a Bronsted base because it produces HO\(^-(aq)\) ions in solution.

We define pOH as (-1) times the log of the hydroxide ion concentration. The pH and the pOH of any aqueous solution are related through the \(K_w\).

\[\text{[HO}^-(aq)] = 10^{-7} \text{ M}\]

\[\text{pOH} = -\log(10^{-7}) = 7\]

\[K_w = [\text{H}^+(aq)][\text{HO}^-(aq)]\]

\[-\log(K_w) = -\log([\text{H}^+(aq)][\text{HO}^-(aq)])\]

\[-\log(10^{-14}) = (-\log[\text{H}^+(aq)]) + (-\log[\text{HO}^-(aq)])\]

\[14 = \text{pH} + \text{pOH}\]