

1.2.2: Hydrogen Bonding

A hydrogen bond is a special type of dipole-dipole attraction which occurs when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. These bonds are generally stronger than ordinary [dipole-dipole](#) and [dispersion forces](#), but weaker than true [covalent](#) and [ionic bonds](#).

Introduction

For a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is the atom to which the hydrogen atom participating in the hydrogen bond is covalently bonded, and is usually a strongly electronegative atom such as N, O, or F. The hydrogen acceptor is the neighboring electronegative ion or molecule, and must possess a lone electron pair in order to form a hydrogen bond.

Since the hydrogen donor is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor, and the lone electron pair on the acceptor.

Types of hydrogen bonds

Hydrogen bonds can occur within one single molecule, between two like molecules, or between two unlike molecules.

- **Intramolecular hydrogen bonds:** Intramolecular hydrogen bonds are those which occur within one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor and an acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.
- **Intermolecular hydrogen bonds:** Intermolecular hydrogen bonds occur between separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present and in positions in which they can interact. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.

Properties and effects of hydrogen bonds

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces. Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

We see that H_2O , HF , and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O , HF , and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF , but partakes in more hydrogen bonds per molecule, so its boiling point is consequently higher.

Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the [viscosity](#) of certain substances. Those substances which are capable of forming hydrogen bonds tend to have a higher viscosity than those that do not. Substances which have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

- **Electronegativity:** Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3 , which do not partake in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, no dipole moment occurs. This prevents the hydrogen bonding from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule (see [Polarizability](#))
- **Atom Size:** The size of donors and acceptors can also effect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve

close proximity when they interact, resulting in a weak interaction.

Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the [unusual properties of water](#). In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain which comprises the wall of plant cells. This creates a sort of capillary tube which allows for [capillary action](#) to occur since the vessel is relatively small. This mechanism allows plants to pull water up into their roots. Furthermore, hydrogen bonding can create a long chain of water molecules which can overcome the force of gravity and travel up to the high altitudes of leaves.

Proteins

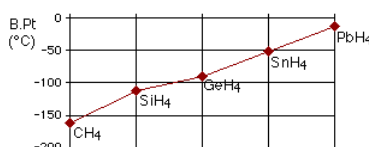
Hydrogen bonding is present abundantly in the secondary structure of [proteins](#), and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain Nitrogen-Hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and visa-versa. Though they are relatively weak, these bonds offer great stability to secondary protein structure because they repeat a great number of times.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe and further reinforce conformation.

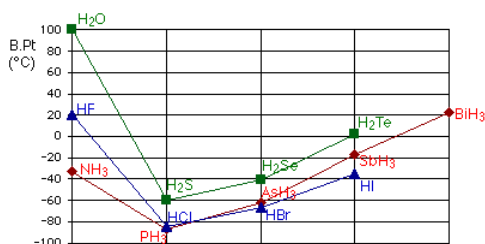
This page explains the origin of hydrogen bonding - a relatively strong form of intermolecular attraction.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the [Group 4 elements](#) with hydrogen, you find that the boiling points increase as you go down the group.



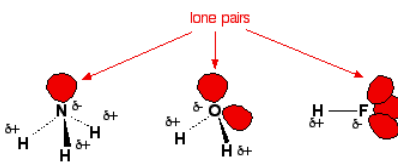
The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals [dispersion forces](#) become greater. If you repeat this exercise with the compounds of the elements in Groups 5, 6 and 7 with hydrogen, something odd happens.



Although for the most part the trend is exactly the same as in group 4 (for exactly the same reasons), the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH₃, H₂O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break. These relatively powerful intermolecular forces are described as hydrogen bonds.

The origin of hydrogen bonding

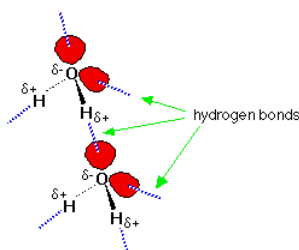
The molecules which have this extra bonding are:



The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you. Notice that in each of these molecules:

- The hydrogen is attached directly to one of the most electronegative elements, causing the hydrogen to acquire a significant amount of positive charge.
- Each of the elements to which the hydrogen is attached is not only significantly negative, but also has at least one "active" lone pair.
- Lone pairs at the 2-level have the electrons contained in a relatively small volume of space which therefore has a high density of negative charge. Lone pairs at higher levels are more diffuse and not so attractive to positive things.

Consider two water molecules coming close together.

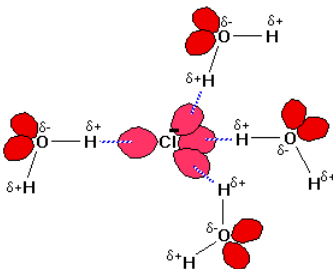


The δ^+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are being constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water as a "perfect" example of hydrogen bonding

Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules. There are exactly the right numbers of δ^+ hydrogens and lone pairs so that every one of them can be involved in hydrogen bonding. This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there aren't enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, there are exactly the right number of each. Water could be considered as the "perfect" hydrogen bonded system.

The diagram shows the potential hydrogen bonds formed to a chloride ion, Cl^- . Although the lone pairs in the chloride ion are at the 3-level and wouldn't normally be active enough to form hydrogen bonds, in this case they are made more attractive by the full negative charge on the chlorine.

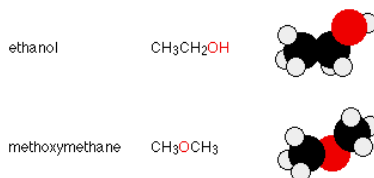


However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An **alcohol** is an organic molecule containing an -O-H group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Such molecules will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier", and more heat is necessary to separate them.

Ethanol, $\text{CH}_3\text{CH}_2\text{-O-H}$, and methoxymethane, $\text{CH}_3\text{-O-CH}_3$, both have the same molecular formula, $\text{C}_2\text{H}_6\text{O}$.



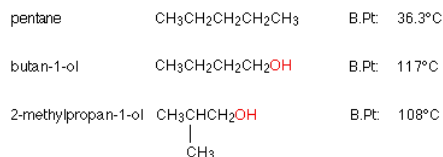
They have the same number of electrons, and a similar length to the molecule. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be much the same. However, ethanol has a hydrogen atom attached directly to an oxygen - and that oxygen still has exactly the same two lone pairs as in a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient δ^+ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens aren't sufficiently δ^+ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C.

It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two are much the same length. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding due to the hydrogen attached directly to the oxygen - but they are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

Hydrogen bonding in nitrogen containing organic molecules

Hydrogen bonding also occurs in organic molecules containing N-H groups - in the same sort of way that it occurs in ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and **DNA**. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Contributors and Attributions

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