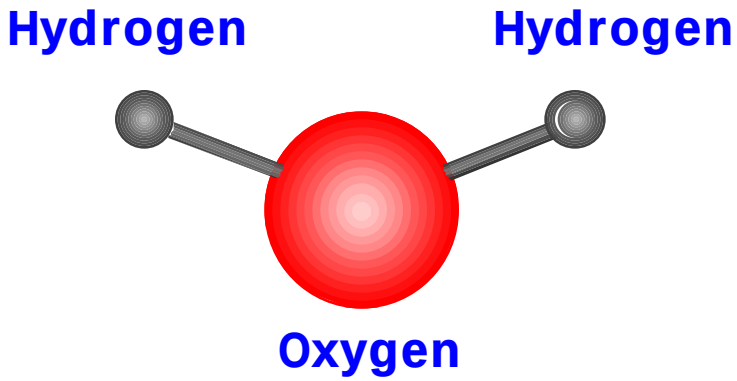
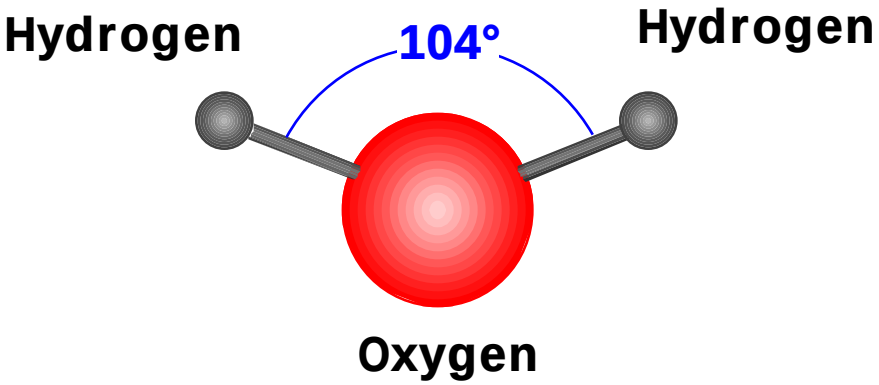
Hydrogen Disorder in Ice

What is Ice Made of ?

Ice is made from water molecules, H_2O. The structure of water molecules in ice is essentially the same as in the vapour. The simplest way to think of a water molecule is like in the picture below.



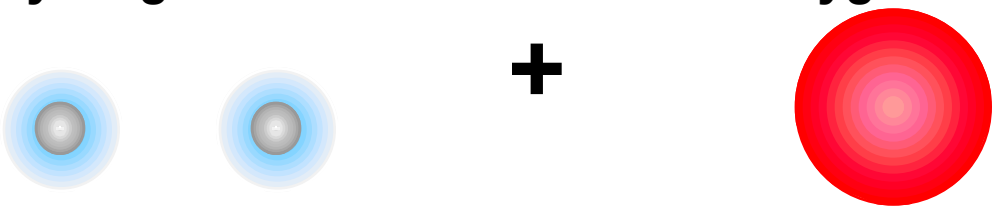
It is important to notice that water molecules are bent.



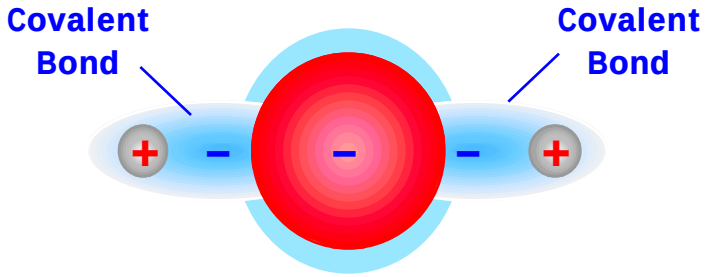
Why is a water molecule that funny shape?

1. A water molecule is made of ...

2 Hydrogen atoms + 1 Oxygen atom

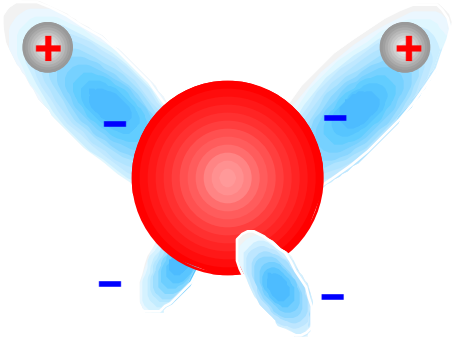


2. The electric field around the Oxygen atom is stronger than that around the Hydrogen. The electrons from the Hydrogen atoms are drawn close to the Oxygen. This leaves the Hydrogen atoms positively charged. The region between the Oxygen and the Hydrogen is known as a Covalent bond ...



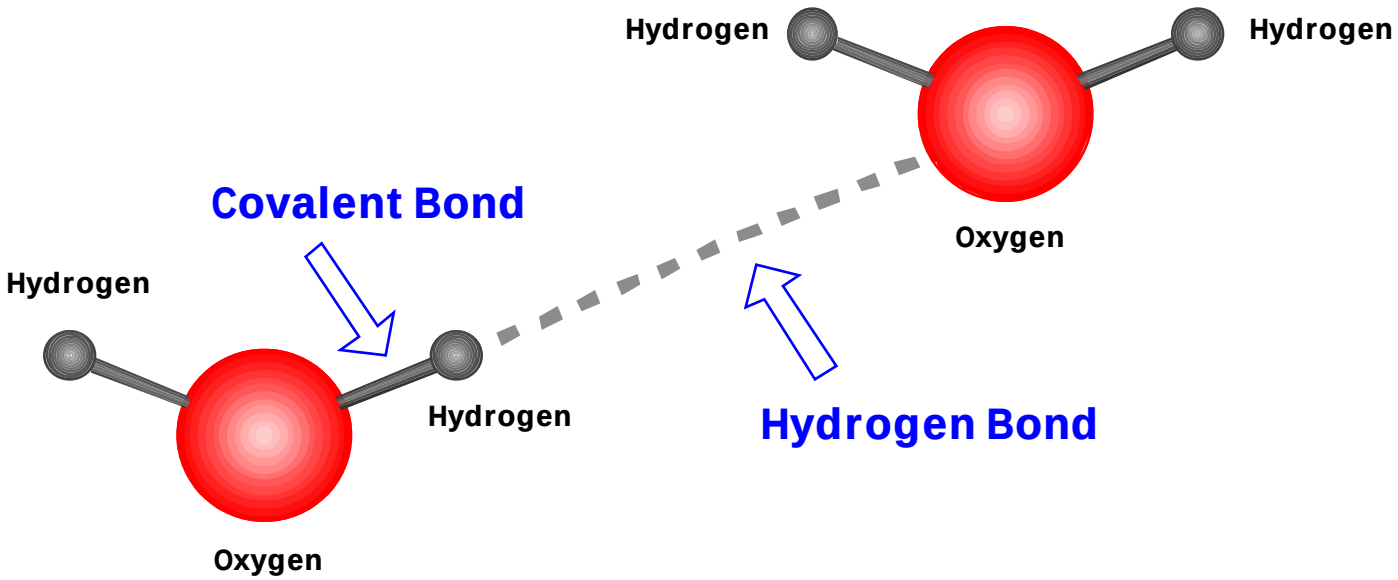
3. The electrons near the Oxygen arrange themselves so as to stay as far away from one another as possible. This minimises their mutual electric repulsion.

The small electron 'lobes' arranged tetrahedrally with respect to the Hydrogens are called a 'lone pair'.



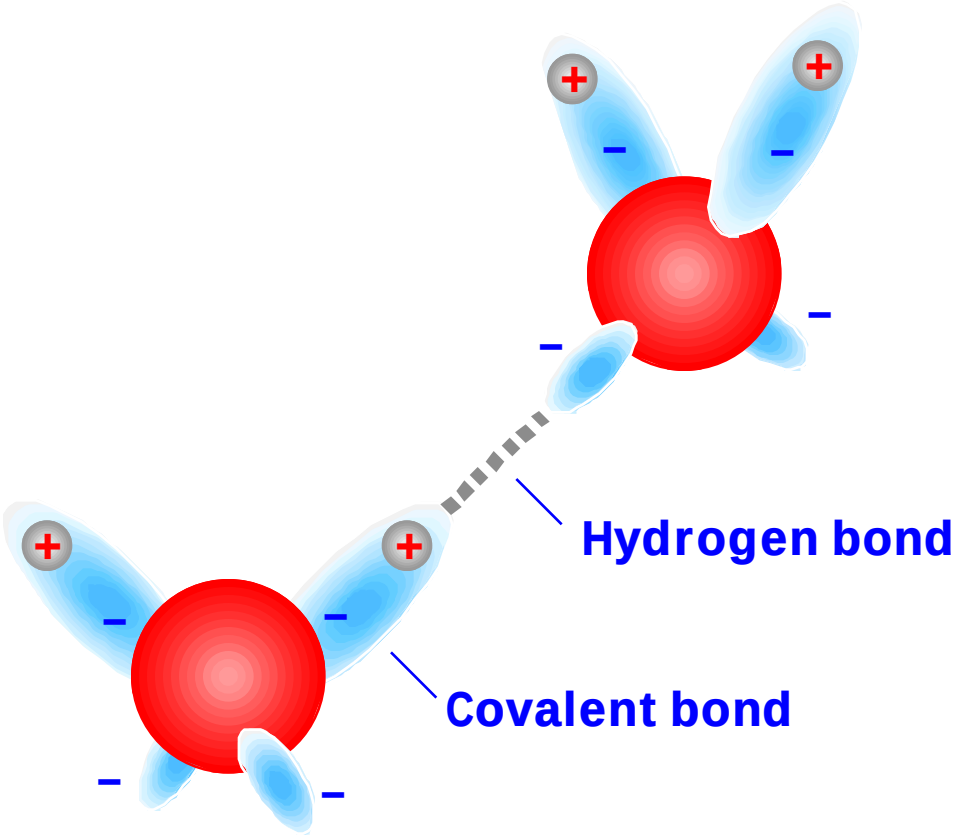
What holds the molecules together in Ice?

In ice the Oxygens are "linked" to each other by the combination of a covalent bond + a hydrogen bond



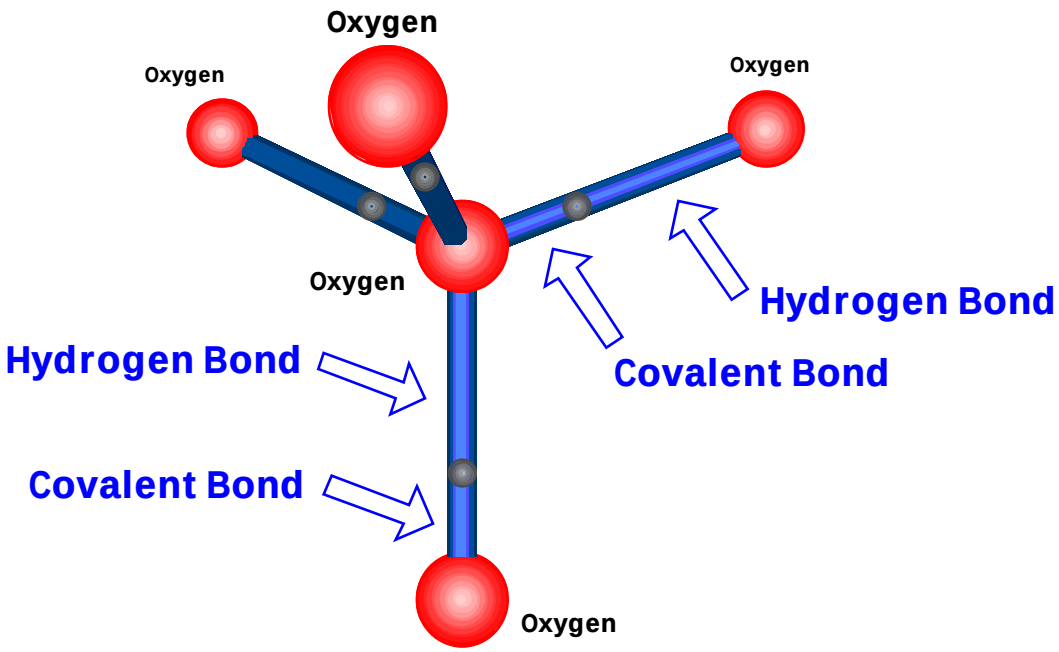
What is a Hydrogen bond?

A Hydrogen bond can be thought of simply as the attraction between the positively charged hydrogen and the negatively charged lone pair electrons.

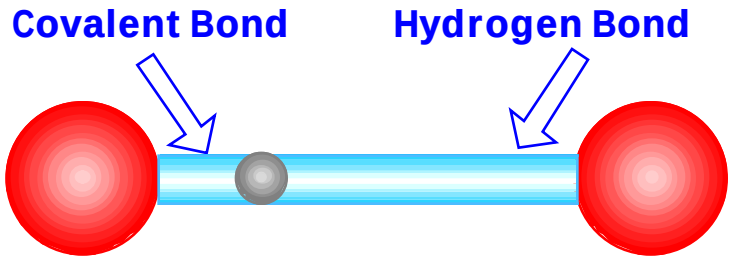


How are the molecules arranged in Ice ?

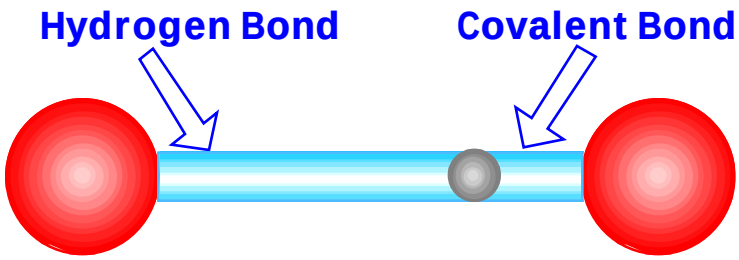
Each Oxygen is "linked" in by a combination of a covalent bond and a hydrogen bond to 4 other Oxygens.



Notice that each Oxygen can be linked to another Oxygen in one of two ways.



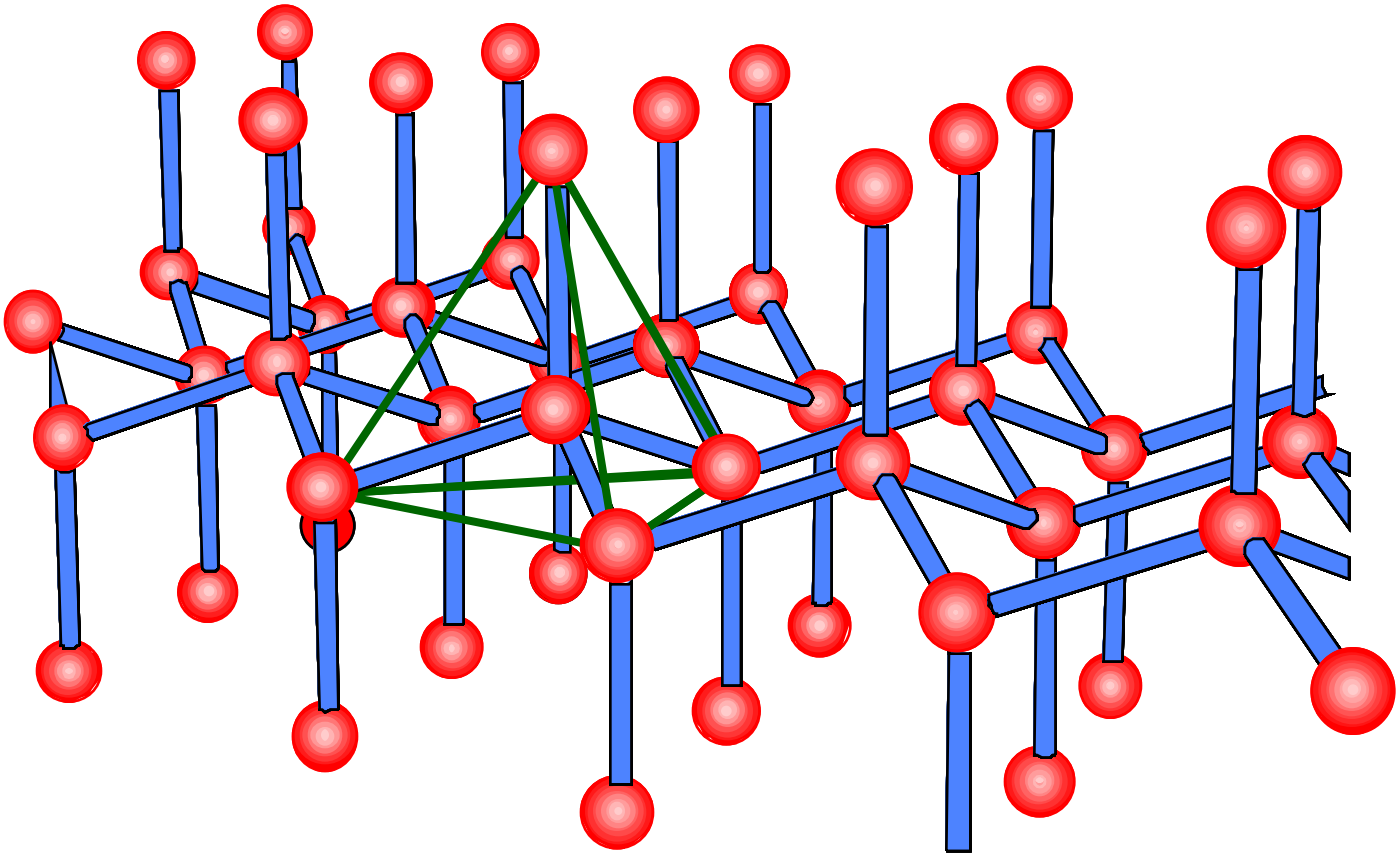
or



How can I understand the structure of Ice?

Forget the Hydrogens!

Ice structures can be thought of in terms of the underlying tetrahedral arrangement of the Oxygens. The tetrahedral arrangement results directly from the "funny shape" of water molecule.



The Oxygen=Oxygen links form the structural framework for all the ice structures. In many ice structures (including normal ice) the hydrogens are distributed at random throughout the Oxygen=Oxygen framework subject to two rules (due to Bernal and Fowler)

1. Only one Hydrogen on each Oxygen=Oxygen link

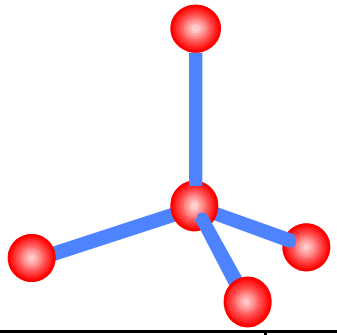
2. There must be two Hydrogens associated with each Oxygen (it is H2O after all).

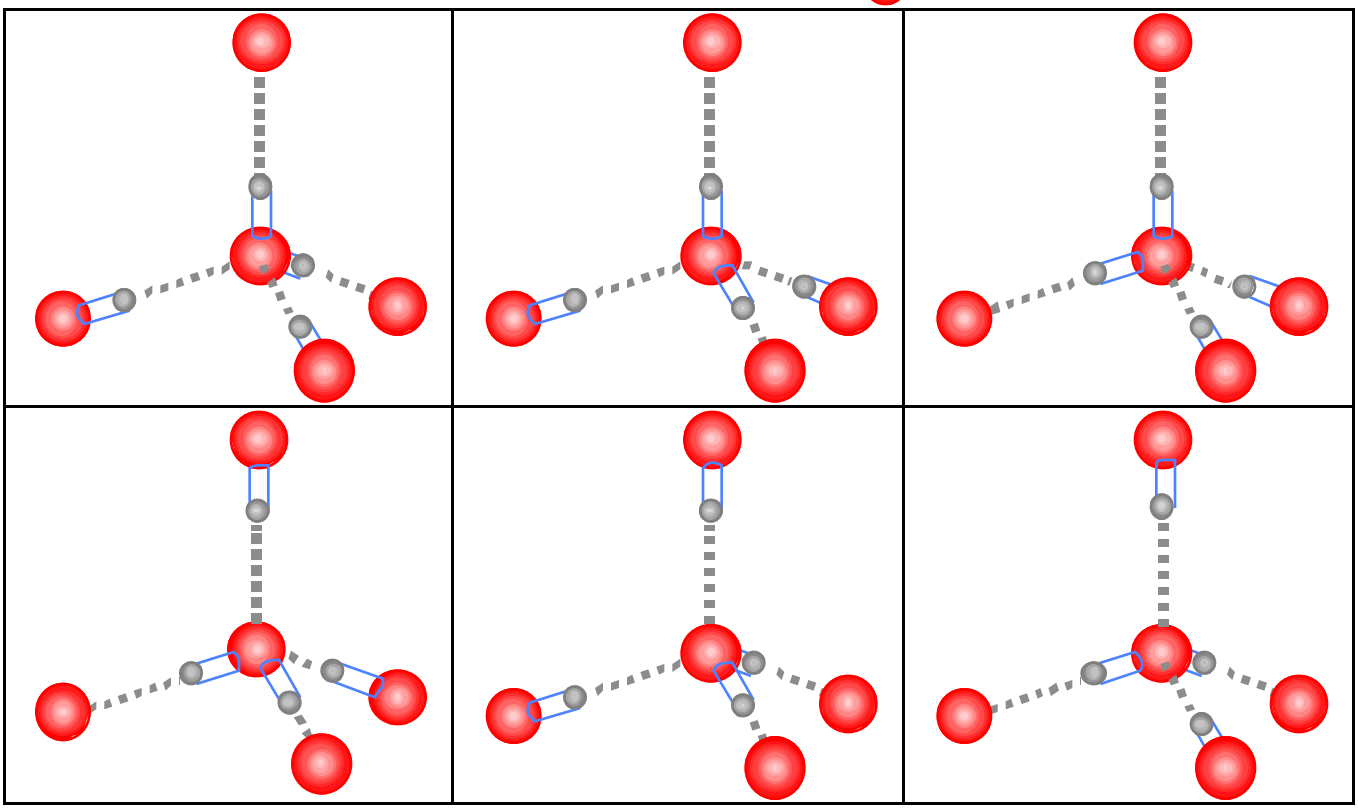
How can I understand the properties of Ice?

Remember the Hydrogens!

In order to understand many properties of ice it is necessary to think in detail about the disorder of the hydrogens. For example, in order to understand the way in which ice responds to applied electric fields (i.e. its electrical conductivity and dielectric constant), one needs to understand how the hydrogens can move.

In each tetrahedral unit there are 6 different ways to arrange the Hydrogens.

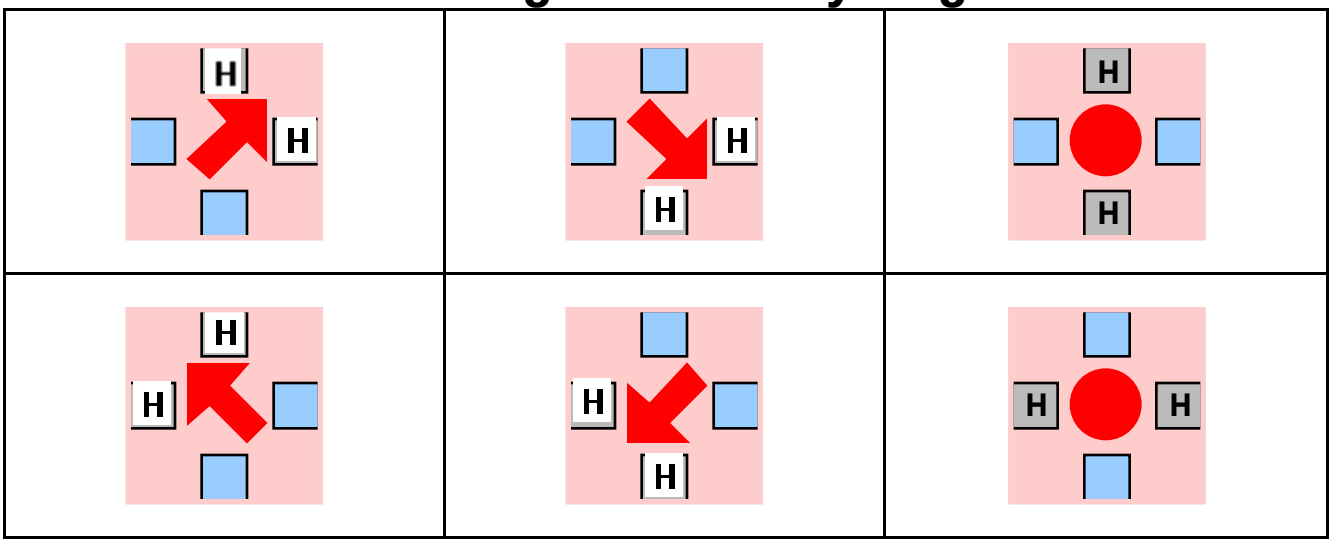




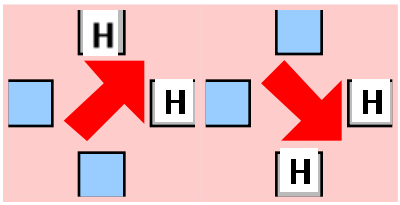
In order to move from one arrangement to another, there must be a 'defect' in the structure. Otherwise all

A Two-Dimensional Analogy

Consider the six "jigsaw" pieces below to be analogous to the different arrangements of hydrogen in ice.



In order to make an "ice" structure you need to place the pieces so that a grey [H] matches a blue lone pair ▭

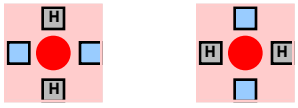


This builds a "square" oxygen framework rather than a tetrahedral one, but some aspects of the physics remain the same.

A Game & A Challenge

Using the six pieces above, construct:

1. **An ordered structure using pieces with circles**



2. **An ordered structure using pieces with arrows**

3. **Using all types of pieces chosen randomly, make two disordered structures, one with 'defects' and one**

What happens at Absolute Zero?

The third law of thermodynamics states (roughly speaking) that there is no disorder in a substance in equilibrium at the absolute zero of temperature. In that case we might expect that when we cool ice, the random arrangement of the hydrogens in ice should be replaced by an ordered arrangement. In fact, this does not happen.

Why don't the hydrogens order ?

1. As the temperature falls, the motion of defects in the hydrogen arrangement becomes slower. i.e. they move through the ice less quickly.

2. Remember that a defect is necessary in order to allow the hydrogens to move about the oxygens. Since the defects move less quickly, the rate at which hydrogens can order becomes very slow.

3. By the time the equilibrium state of the hydrogens would like to become order, there are essentially no mobile defects and the ice is "stuck" in the disordered state.

Can one make the hydrogens order ?

Yes. By introducing small amounts of impurities that provide a different type of defect, it is possible to "trick" ice into entering a new order structure, Ice eleven (Ice XI)