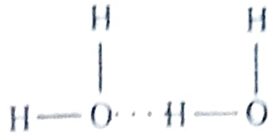
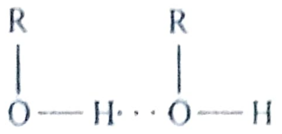
Hydrogen bonding :

When a hydrogen atom lies between two atoms having strong elecronegativies, it shows an unique property of forming a bond between the two electronegative atoms. One is held by a covalent bond and the other by an electrostatic force. This electrostatic force is called the hydrogen bond. Hydrogen bond is usually indicated by dotted lines. Hydrogen bond is formed in the following compounds.

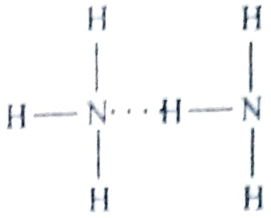
Hydrogen fluoride



Water



Alcohol



Ammonia

. . . . = Hydrogen bond

Hydrogen bond may be represented by the general formula A – H ... B. One of the essential conditions of hydrogen bond is that, both atoms A and B which are bridged by hydrogen must be highly electronegative elements and small in size. Another condition is that must have a lone pair of electrons. Thus hydrogen bond is seen only compounds of fluorine, oxygen and nitrogen.

Nature of hydrogen bonding

Hydrogen bond is electrostatic in nature. All molecules which enter into hydrogen bonding are strongly polar. Consider hydrogen fluroide.

$$^{\delta+}H \rightarrow - F^{\delta-}$$

Fluorine atom has a fractional negative charge and hydrogen atom has fractional positive charge. This is because fluorine is highly electronegative when two HF molecules approach closely, there would be strong electrostatic attraction between the positively charaged hydrogen of one of the molecules and the negatively charged fluorine atom of the other molecule. Thus hydrogen bridges the two fluorine atoms, one of them by covalent link and the other by hydrogen bond.

H – F .... H – F

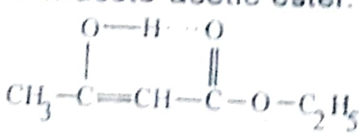
Hydrogen bond is much weaker than a normal covalent bond. The strength of hydrogen bond has been found to vary between 2 – 10k cals per mole (The covalent bond has been found to be of the order 100k cals. per mole.)

Types :

There are two types of hydrogen bonds,

1. Inter molecular hydrogen and
2. Intra molecular hydrogen bond.

The inter - molecular hydrogen bond is formed between two molecules. e.g., H – F .... H – F .... H – F. This leads to molecular association. The **intramolecular hydrogen bond** is formed between atoms within the same molecule. For example, intramolecular hydrogen bond is found in aceto acetic ester.



This leads to the formation of a ring known as chelate ring (such rings are usually six membered).

Inter molecular hydrogen bonding leads to molecular association. This results in an increase in the boiling point or melting point. Intramolecular hydrogen bonding does not lead to molecular association. Hence compounds with intramolecular hydrogen bonding have low boiling and melting points.

Effect on properties :

1. ***Abnormal boling points :***

Let us consider the boiling points of compounds of hydrogen with various elements of Group V, VI, and VII.

From table 1 it is seen that hte boiling points of all compounds except the first compound in each group increases with an increase the molecular weight. NH_3 which has the lowest molecular weight is expected to have the lowest boiling point.

Table

Group V			Group VI			Group VII		
For. mula	Mol. wt.	B.Pt. °C	For mula	Mol wt.	B.Pt. °C	For mula	Mol. wt.	B.Pt. °C
NH_3	17	13	H_2O	18	100	HF	20	19.4
PH_3	34	85	H_2S	34	- 59.6	HCl	36.5	-85
AsH_3	78	55	H_2Se	81	- 42	HBr	81	-67
SbH_3	125	17	H_2Te	130	-1.8	HI	128	-35.5

But it has an abnormally high boiling point of –33°C. Similarly H_2O with the molecular weight 18 has the boiling point 100°C, where as, all other compounds with higher molecular weights than water have low boiling points. These abnormal boiling points of NH_3, H_2O and HF are due to the intermolecular hydrogen bond which leads to the association of molecules.

Thus intermolecular hydrogen bonding and the consquent molecular association is the reason for the following observations.

i. At room temperature H_2O is a liquid while H_2S is a gas / water boils at a higher temperature than hydrogen sulphide.

ii. alcohols are high boiling liquids.

iii. Ammonia has a higher boiling point.

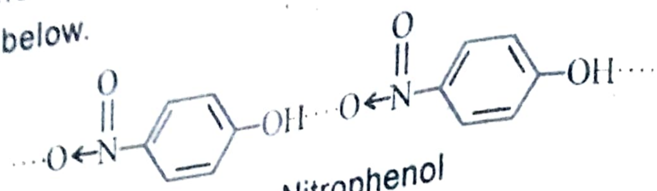
2. ***Density of ice is less than that of water :***

Generally solids have higher density than liquids. But ice has lower density than liquid water. As water is warmed from 0°C on wards, more and more hydrogen bonds are broken. Consequently the molecules come closer and closer together. This leads to contraction. Hence the density of water is maximum at 4°C. However there is the normal effect of expansion also as in other liquids. It appears that upto 4°C the contraction predominates expansion. Above 4°C the expansion

predominates and hence there is increase in volume as the temper
rises beyond 4°C. Hence the density decreases.

3. ***p - Nitrophenol has higher boiling point than o - nitrophenol***

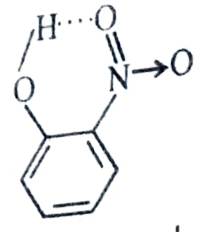
p - Nitrophenol on account of larger distance between
– OH and –NO_2 groups does not show intramolecular hydrogen bond
On the other hand it shows intermolecular hydrogen bonding
illustrated below.



p - Nitrophenol

As a result of intermolecular hydrogen bonding the p - deriva
undergoes association. Hence it has a higher boiling point than
ortho isomer.

On the other hand on account of intermolecular hydrogen bondi
in the o - isomer, no such association is possible. Consquently
ortho derivative is more volatile than the para derivative.



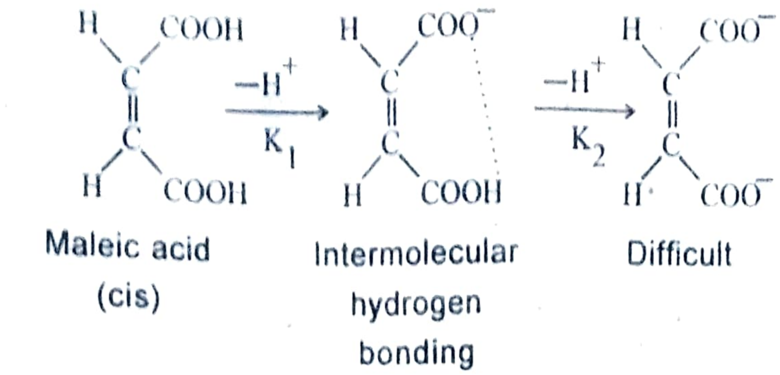
o - Nitrophenol

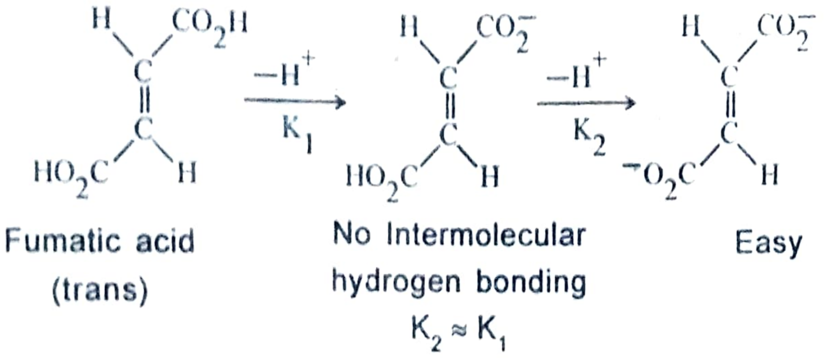
Thus while o - nitrophenol is steam volatile the p - nitrophenol
non - volatile.

It is for the same reason, o - nitrophenol has a lower melting po
and solubility in water than the p - isomer.

4. The second dissociation constant is lesser than the first
dissociation constant in maleic acid while both are same for fumar
acid. This is because the O^- of the anion got after te first H^+ has le
maleic acid, forms an intramolecular hydrgeon bonding with the second
acid H, thereby, making it difficult to dissociate. This becomes possible
because maleic acid is the cis isomer. So the second dissociation of
H^+ becomes difficult resulting in the reduction in the second dissociation
constant.

In furmaric acid no such intramolecular hydrogen bonding is possible in the anionof the first acidic dissociation, as it is the trans isomer. That is why, for fumaric acid both first and second dissociation constants have the same value.





5. ***Solubility of organic compounds :***

It is a famillar fact that the organic compounds are generally insoluble in water. But the lower alcohols, acids, sugars etc. are soluble in water. This is due to the hydrogen bonding. As a rule, if a compound is capable of forming hydrogen bond with water, it dissolves in water.

6. ***Biological process :***

Many biological processes involve hydrogen bonds at one stage or the other. Enzyme action seems to involve hydrogen bonding. Muscle action which is rapid and reversible, involves hydrogen bonding. Contraction is due to the formation of hydrogen bond and relaxation is due to the breaking of hydrogen bond. Memory may be related to the setting up of regular hydrogen bonds in the brain.