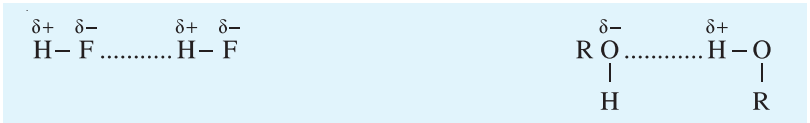
CONCEPT OF HYDROGEN BONDING Section - 4

Molecules that contain F–H, O–H, N–H bonds (e.g., Water, Alcohols, Organic acids, Amines, Aromatic alcohols, etc.) show a strong tendency to associate, i.e., to link up to form larger molecules. This feature exists in solid form and as well as in solutions in certain solvents. In all of such compounds, O–H, or N–H or F–H, bond is highly polar due to large difference in electronegativity. The electrostatic attraction between such molecules should be quite strong. The positive end of one molecule attracts and is strongly attracted by the negative end of the neighbouring molecule. In this manner a large number of molecules are associated to form a cluster of molecules. Since in each case the hydrogen atom is responsible for the formation of linkages, this is known as Hydrogen bond or H–bond. It is impossible for hydrogen to form a second covalent bond so the additional linkage is shown by a dotted line. Hydrogen bonds are always of type : –A–H....B–, where A and B may be atoms of O, F, N. Hydrogen bonds are comparatively weak, with bond energies of 10–30 KJ/mol, but they are widespread and have important effect on many physical properties of many Organic and Inorganic compounds.



Types of H-Bonding :

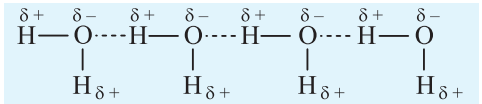
Intermolecular H-Bonding :

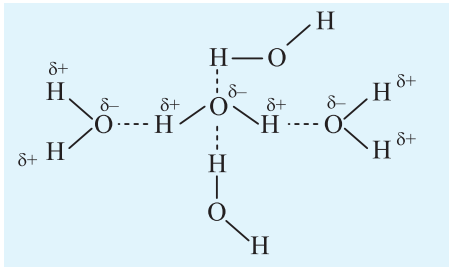
This type of H-bonding takes place between H and electronegative element present in the different molecules of the same substance (as in between H_2O and H_2O) or different substances (as in between H_2O and NH_3).

(a) In water molecules :

Due to polar nature of H_2O, there is association of water molecules giving a liquid state of abnormally high b.p.

If we actually observe, one water molecule is joined to four water molecules, two with H-atoms and other two with O-atom. Thus coordination number of water molecules in water is four as shown in figure :

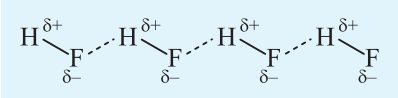




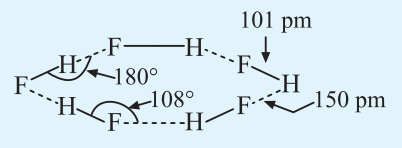
Note : Although many compounds can form intermolecular hydrogen bonds, the difference between H_2O and other polar molecules, such as NH_3 and HF, is that each oxygen atom can form two hydrogen bonds, the same as the number of lone electron pairs on the oxygen atom. Thus, water molecules are joined together in an extensive three-dimensional network in which each oxygen atom is approximately tetrahedrally bonded to four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. This equality in the number of hydrogen atoms and lone pairs is not characteristic of NH_3 or HF or, for that matter, of any other molecule capable of forming hydrogen bonds. Consequently, these other molecules can form rings or chains, but not three-dimensional structure.

When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). Due to this volume of ice is greater than liquid water and thus ice is lighter than water. We can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks hence volume increases and hence density decreases. Thus water has maximum density at 4°C.

(b) In hydrofluoric acid (HF), there is again association by H-bonding.

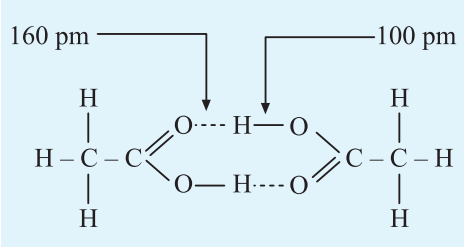


However in the gaseous state, several polymeric forms of the HF molecules exist in which the monomers are held together through H-bonding to form a pentagonal arrangement.

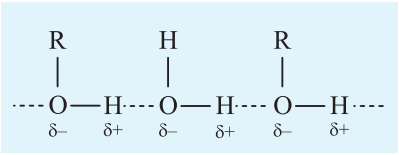


(c) There is also similar H-bonding in alcohol (R — OH) ammonia (NH_3) and phenol (C_6H_5OH) molecules.

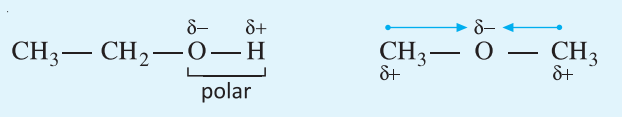
(d) Carboxylic acid dimerizes in gaseous state due to H-bonding.



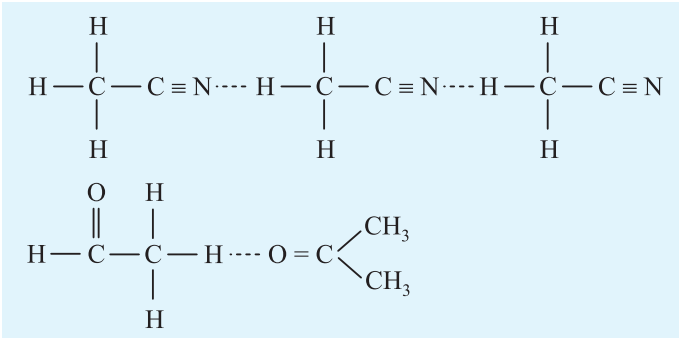
(e) Alcohol is said to be highly soluble in water due to crossed intermolecular H-bonding (between H_2O and R – OH molecules).



However isomeric ether is less soluble in water due to ether's non-polar (or weakly polar) nature.



(f) Though the hydrogen atoms in a methyl groups are not polarized, if an electronegative group like chloro, carbonyl, nitro or cyano is attached to it, the C — H bond gets polarised due to the inductive effect and the hydrogen atom becomes slightly acidic resulting in the formation of weak hydrogen bonds.

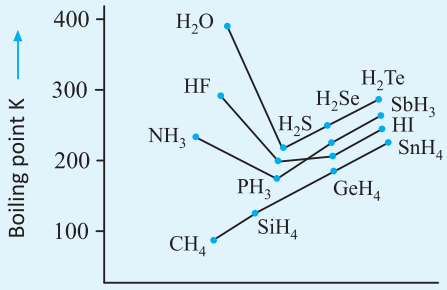


Consequences of the Intermolecular Hydrogen bonding :

(a) Due to H-bonding boiling points of water, ammonia, hydrofluoric acid are abnormally high shown in figure.

(b) Solubility of the organic compounds in water is due to H-bond formation.

(c) Due to hydrogen-bonding, viscosity (η) of the liquid increases as given below in centipoises (CP).



CH_3CH_2OH

$\eta = 2$ CP

CH_2OH
|
CH_2OH

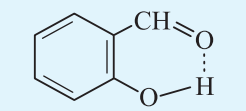
$\eta = 17$ CP

CH_2OH
|
$CHOH$
|
CH_2OH

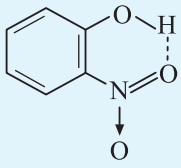
$\eta = 1070$ CP

Intramolecular H-bonding :

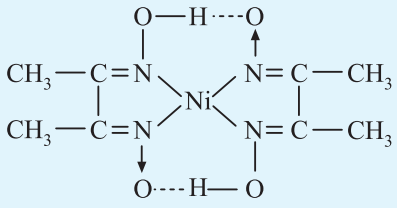
This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.



o-hydroxy benzaldehyde



o-nitro phenol



Nickel dimethyl glyoximate (a chelate)

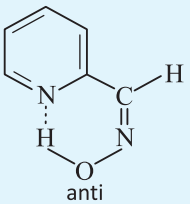
The necessary conditions for the formation of intramolecular hydrogen bonding are :

(a) The ring formed as a result of hydrogen bonding should be planar.

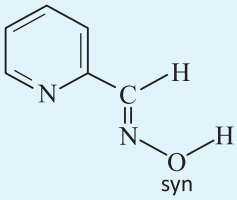
(b) A five or six membered ring should be formed.

(c) Interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

In case of anti-form of pyridine-2-carboxaldoxime there is intramolecular hydrogen bonding but it is not shown in syn-form.



anti



syn

In this type of H–bonding, the bonding occurs within two atoms of same molecule. Such type of bonding generally occurs in aromatic organic compounds. It is also known as Chelation.

Consequences of the Intramolecular Hydrogen bonding :

Presence of Intramolecular H-bonding decreases the boiling points as well as there solubility in water.

(a) Hydrogen bonding between two atoms of the same molecule (intramolecular H-bonding) leads to unavailability of these atoms to bond with atoms of other molecule. In other words intra-molecular H-bonding between atoms of same molecule, makes them unavailable for inter-molecular H-bonding and hence compounds showing such type of bonding tends to show lower boiling points. For example, *o* - Chlorophenol, *o* - Nitrophenol and other *o* - derivatives (isomers) of hydroxy, carbonyl and acids show low boiling as well as melting points as compared to their *m*- or *p* - derivatives (which exhibit intermolecular H-bonding).

(b) The solubility of all such compounds also decreases for the same reason i.e., bonding between atoms of same molecules or chelation, does not allow these molecules to form inter-molecular bonds. For example in *o* - Nitrophenol, O - H group is busy making intramolecular H-bond with O atom of the NO_2 group and becomes unavailable for intermolecular H - bonding and hence it is very less soluble in water.

Illustration - 16 *Why H_2O is liquid while H_2S is a gas at ordinary temperature ?*

SOLUTION :

Oxygen has high electronegativity than sulphur. As a result, H_2O forms hydrogen bonding. Consequently, molecules of water come nearer to each other through hydrogen bonding. This result is higher boiling point of water and hence it is a liquid.

Illustration - 17 *The density of ice is less than that of water or ice floats over water. Explain.*

SOLUTION :

In ice, water molecule is associated with four other molecules through hydrogen bonding in a tetrahedral manner, i.e., it has open-cage like structure in which lesser molecules are packed per unit volume. When ice melts, the molecules come closer to one another. Consequently the density of water in liquid state is more than solid state. Thus, ice floats over water.

Illustration - 18 *The boiling point of H_2O is more than the boiling point of HF although fluorine is more electronegative than oxygen and form stronger H-bond.*

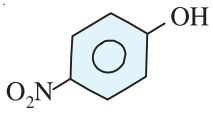
SOLUTION :

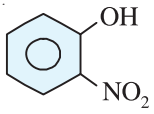
The strength of a hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom and the hydrogen nucleus. Fluorine is more electronegative than oxygen, and so we would expect a stronger hydrogen bond to exist in liquid HF than in H_2O. But boiling point of HF is lower than that of water because each H_2O takes part in four intermolecular hydrogen bonds. Therefore, the forces holding the molecules together are stronger in H_2O than in HF.

IN-CHAPTER EXERCISE-B

Choose the correct option for each of the following questions. Only one option is correct.

1. Out of the two compounds shown below, the vapour pressure of II at a particular temperature is expected to be:

I. 

II. 

(A) higher than that of I
(B) lower than that of I
(C) same as that of I
(D) can be higher or lower depending upon the size of the vessel

2. Out of $CHCl_3$, CH_4 and SF_4 the molecules having regular geometry are:
(A) $CHCl_3$ only **(B)** $CHCl_3$ and SF_4
(C) CH_4 only **(D)** CH_4 and SF_4

3. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order :
(A) $NH_2^- > NH_3 > NH_4^+$
(B) $NH_4^+ > NH_3 > NH_2^-$
(C) $NH_3 > NH_2^- > NH_4^+$
(D) $NH_3 > NH_4^+ > NH_2^-$

4. Which of the following bonds is the strongest ?
(A) F–F **(B)** I–I
(C) Cl–Cl **(D)** Br–Br

5. Which one of the following hydrogen halides has the lowest boiling point?
(A) HF **(B)** HCl
(C) HBr **(D)** HI

6. Among the following ions, the $p\pi - d\pi$ overlap could be present in:
(A) NO_3^- **(B)** PO_4^{3-}
(C) CO_3^{2-} **(D)** NO_2^-

7. Which of the following is soluble in water :
(A) CS_2 **(B)** C_2H_5OH
(C) CCl_4 **(D)** $CHCl_3$

8. Among the following, the paramagnetic compound is :
(A) Na_2O_2 **(B)** O_3 **(C)** N_2O **(D)** KO_2

***9.** Which of the following have identical bond order ?
(A) CN^- **(B)** O_2^- **(C)** NO^+ **(D)** CN^+

10. The species having bond order different from that in CO is :
(A) NO^- **(B)** NO^+ **(C)** CN^- **(D)** N_2

11. Using MO theory predict which of the following species has the shortest bond length ?
(A) O_2^- **(B)** O_2^{2-} **(C)** O_2^{2+} **(D)** O_2^+

12. The ion that is isoelectronic with CO is :
(A) CN^- **(B)** O_2^+ **(C)** O_2^- **(D)** N_2^+

13. Which one among the following does not have the hydrogen bond ?
(A) phenol **(B)** liquid NH_3
(C) water **(D)** liquid HCl

14. The molecule having one unpaired electrons is :
(A) NO **(B)** CO **(C)** CN^- **(D)** O_2

15. The hydrogen bond is strongest in :
(A) O – H .....S **(B)** S – H ....O
(C) F – H ..... F **(D)** F – H ..... O

16. Hydrogen bonding is maximum in :
(A) Ethanol **(B)** Diethylether
(C) Ethyl chloride **(D)** Triethylamine

17. The maximum possible number of hydrogen bonds a water molecule can from is :
(A) 2 **(B)** 4 **(C)** 3 **(D)** 1

18. The number and type bonds between two carbon atoms in CaC_2 are :
(A) one sigma (σ) and one pi (π) bonds
(B) one sigma (σ) and two pi (π) bonds
(C) one sigma (σ) and one and a half pi (π) bonds
(D) one sigma (σ) bond.

19. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in :
(A) NO_2^+ and BaO_2 **(B)** KO_2 and AlO_2^-
(C) KO_2 only **(D)** BaO_2 only

20. The common features among the species CN^-, CO and NO^+ are :

(A) bond order three and isoelectronic
(B) bond order three and paramagnetic
(C) bond order two and diamagnetic
(D) isoelectronic and electron deficient

21. Which of the following molecular species has unpaired electron(s) ?

(A) N_2 **(B)** F_2
(C) O_2^- **(D)** O_2^{2-}

22. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+

(A) Paramagnetic and Bond order < O_2
(B) Paramagnetic and Bond order > O_2
(C) Diamagnetic and Bond order < O_2
(D) Diamagnetic and Bond order > O_2

23. In solid argon, the atoms are held together by

(A) Ionic bonds
(B) Hydrogen bonds
(C) Vander Waals forces
(D) Hydrophobic forces

24. Which of the following exhibits the weakest intermolecular forces?

(A) He **(B)** HCl
(C) NH_3 **(D)** H_2O

25. Among the following the weakest force of interaction is

(A) Metallic bond
(B) Ionic bond
(C) Van der Waal's force
(D) Covalent bond

26. Pure covalent molecules are usually held in a crystal structure by

(A) Dipole-dipole attraction
(B) Electrostatic attraction
(C) Hydrogen bonds
(D) Vander Waal's attraction

27. Which inert gas possesses the highest polarizability?

(A) He **(B)** Ne
(C) Ar **(D)** Xe

28. Dissolution of iodine crystals in carbon tetrachloride solvent can be attributed to

(A) Hydrogen bonding between them
(B) dipole- induced dipole interaction between them
(C) London dispersion forces between them
(D) Large molecular mass of Iodine and hence large van-der waals forces

29. If NaCl dissolves in water then the nature of interaction between them is

(A) Dipole-Dipole interaction
(B) Dipole- Induced dipole interaction
(C) Ion- dipole interaction
(D) Hydrogen Bonding

30. The attractive forces that exist between non polar molecules such as O_2, N_2 or mono-atomic gases like He, Ne are called

(A) hydrogen bond forces
(B) dispersion forces
(C) dipole - dipole forces
(D) ion-dipole forces

31. Which of these is correct regarding a hydrogen bond?

(A) These have a reasonable effect on the structure and properties of a compound
(B) Hydrogen atoms attached to N, O or F is able to inter-pose itself between electronegative atoms bonding them together
(C) The heat of a hydrogen bond can be 40 kJ/mole
(D) All of these are correct

32. Which of these can explain the unusual contraction of water when heated between 0°C to 4°C?

(A) Hydrogen bonding
(B) Covalent nature of water
(C) Permanent dipole moment in water
(D) Lesser density of ice as compared to water