

HYDROGEN BONDING AND WEAK INTERMOLECULAR FORCES

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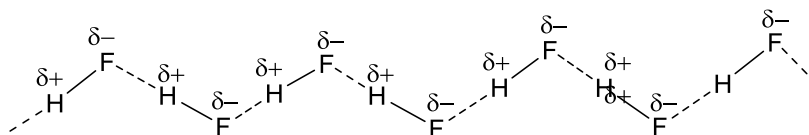
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Hydrogen Bonds:

The hydrogen bond may be defined as a weak electrostatic force of attraction that operate between a hydrogen atom that is covalently bonded to an atom of high electronegativity and smaller size such as F, O and N (as donor atom). Hydrogen bond are larger than covalent bond and much weaker; there strengths lie in range 5-42 kcal/mole. The covalent bond between a hydrogen atom and electronegative element is considerably polar because the electronegative attract the bonding electron towards itself. The positive character charge developed on hydrogen atoms which attract the partial negative charge of the second electronegative atom (of the same or different molecule) forming a bond that is called H-bond. **Hydrogen bond is thus a special type of dipole-dipole interaction.**

For example, H-F molecules are held together by hydrogen bonding (represented by dotted lines) as shown below. Hydrogen bond distance range is about 2.6-3.1 Å



(Intermolecular H-bonding in HF molecule: zig-zag nature)

Some H-bond energies are listed below;

Type of bond	Mean energy kcal/mole
O—H---N	7
O—H---O	6
C—H---O	2.6
N—H---O	2.3
N—H---N	2 - 4
N—H---F	5
F—H---F	7

✓ Secondary interactions in H-bonding systems:

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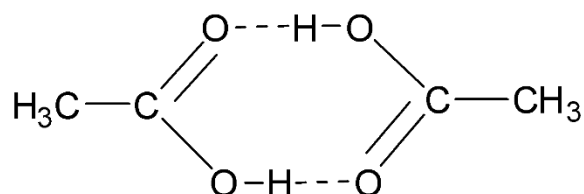
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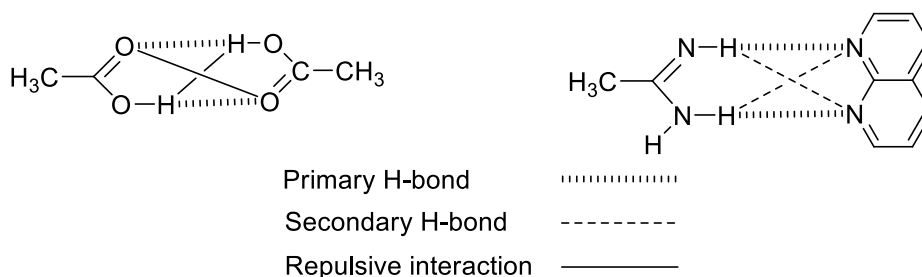
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Since the microenvironment near hydrogen bonds greatly influences their strength, it makes sense that the proximity of other hydrogen bonds would also have an influence. In fact, when there are hydrogen bonds adjacent to one another, secondary interactions can arise which can either reinforce or weaken the primary hydrogen bonds. For example, the dimerization of two carboxylic acids (in vapour phase) yields two hydrogen bonds. However, there are also two "transannular" repulsive interactions between the hydrogen bonded species. Electrostatic arguments nicely rationalize these. In this system, the hydrogens are $\delta+$, the oxygens $\delta-$, and so the $H\cdots H$ and $O\cdots O$ interactions are repulsive. In contrast, when the donors are on one structure, and the acceptors on the other, the primary hydrogen bonds are supported by the secondary interactions:



Dimerization of acetic acid



Acetic acid is found to be dimer due to such type- hydrogen bonding.

- **Detection of H-bond:**

- ✓ For a hydrogen bond of the type $X-F\cdots Y$, X to Y distances are found (by X-ray study) to be shorter than the sum of their Van der Waals radii. This is indicative of the presence of a H-bond.
- ✓ When X H group enters into H-bonding the X -H stretching frequency is lower in the IR spectrum of the compound.

In shortly:

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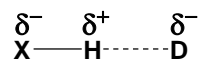
- Hydrogen bond is an attractive force between hydrogen which is attached with more electronegative atom more electronegative atom or ion.
- Hydrogen bond energy ~ 8-42 kJ/mol (where as covalent bond energy ~ 200-450 kJ/mol)
- More electronegative atom like F, O, N generally form hydrogen bond.
- N, Cl has same electronegativity, but nitrogen form hydrogen bond due to its smaller size.
- Electronegativity difference is higher between hydrogen and electronegative atom, the strength of hydrogen atom is higher.
- **It is 3c-4e (linear type) bonding.**
- Weak dipole-dipole interaction
- **Strongest H- bonding found in symmetrical HF₂⁻**
- Hydrogen bond is directional in nature.
- The electronegativity of Cl is not so much high due to higher size factor that the extend of bond polarization in HCl is not sufficient to form H-bonding like HF molecule.

❖ **Factor affecting H-bonding:**

- **The energy of hydrogen bond in the order: (see above table)**

H---F>H---O>H---N	Electronegativity
(F-H---F) > (OH---O) > (NH---N)	F=4.0; O=3.5; N=3.0

Based on:



X = F, O, N

D (donor atom) = F, O, N

- Bond polarity of the covalent bond in H-X system (X = F, O, N) (higher electronegativity of X higher will be bond polarity and thereby hydrogen bonding ability will increase)
- Electronegativity of donor atom: higher the electronegativity of the adjacent donor atom higher will be H-bonding.

Stronger the H-bonding, stronger will be the corresponding bond-dissociation energy enthalpy.
Strongest H-bonding found in HF₂⁻.

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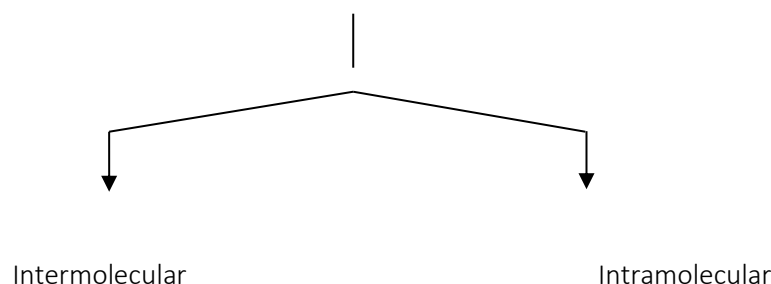
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❖ Types:

Two type of hydrogen bond are existed, one is *Intermolecular* hydrogen bond another is *intramolecular* hydrogen bond.

Hydrogen Bond



- **Intermolecular:** When hydrogen bond is formed between the two molecules then such type H-bond is called intermolecular H-bond. Such as, water, ammonia and hydrofluoric acid, *para*-nitrophenol etc.

Intermolecular hydrogen bonding increases the molecular association or aggregation force hence hydrogen bonded (intermolecular) molecule will have higher boiling point than the non hydrogen bonded molecule. Alcohol have higher boiling point than the isomeric ethers.

In intramolecular hydrogen bonding many molecules are associated together to form a giant molecule for which their boiling point becomes higher.

- **Intramolecular:** When hydrogen bond is formed within same molecule then such type H-bond is called intramolecular H-bond. Such as, salicylic acid, salicylaldehyde, *ortho*-nitrophenol.

The necessary conditions for the formation of intramolecular hydrogen bonding are

- a. The ring formed as a result of H-bonding should be planer;
- b. A five or six- membered ring should be formed (through chelation)
- c. Interacting atoms should be placed in such a way that there is minimum strain during the closure.

Condition (c) is apparent only when stereochemical rigid molecule are considered. Thus, the '*anti*' form of pyridine-2- carboxaldoxime is intramolecular hydrogen bonded, whereas the '*syn*' form can not form as the lone on the pyridine 'N' atom is not oriented towards the -OH group of the oxime.

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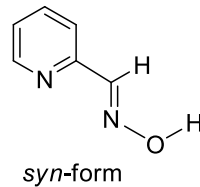
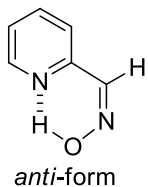
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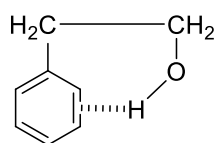
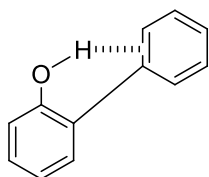
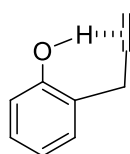
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Intramolecular H-bonds occur between an -OH group and the π -electron of benzene ring or of an ethylenic bond and intermolecular H-bond arise

between CDCl_3 and the benzene ring when CDCl_3 is dissolve in benzene.



When the -OH group of a hydroxilic compound is tied up by chelation, association with water is hindered and the water solubility then approaches that of a similar compound which lacks the -OH group.

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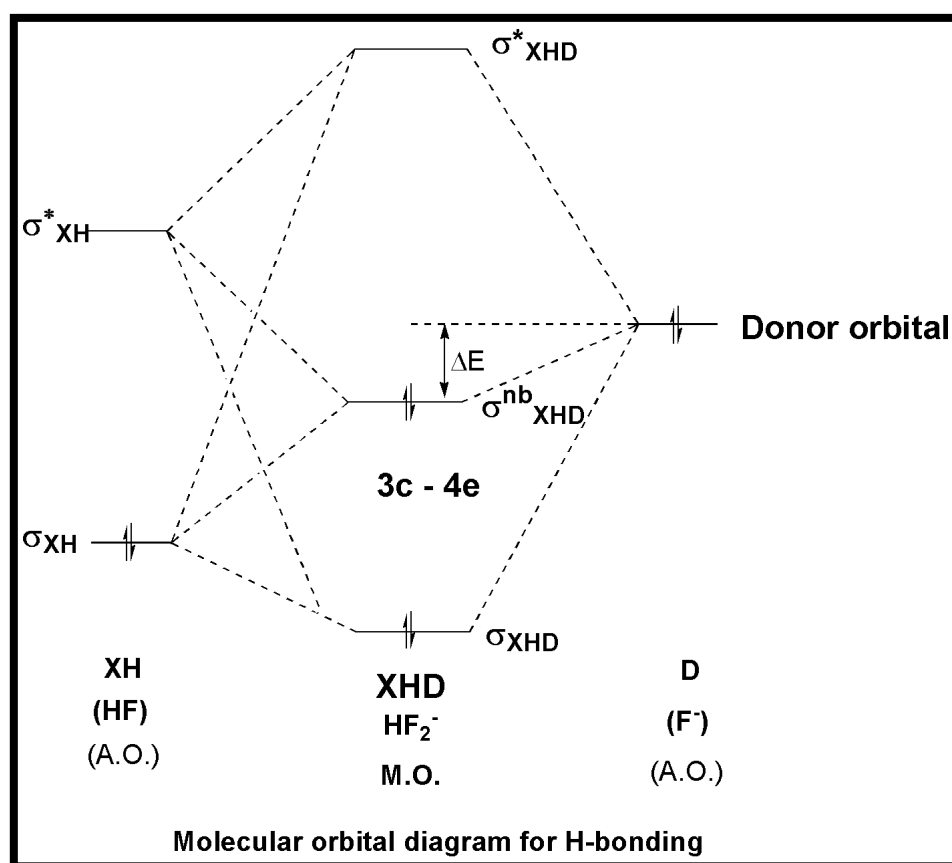
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- Molecular orbital (M.O.) approach of H-bonding:

Hydrogen bonding represented as, X-H.....D represents the interaction between the donor species D, and the acceptor species X-H, through the H-end. The resultant molecular orbitals (MOs) in the adduct are formed by the linear combination of three orbitals: δ (filled) and δ^* (vacant) of HX and sp^n hybrid orbital (i.e. lone pair residing on D) of D. It leads to three-centred MOs in which four electrons are accommodate in the bonding and nonbonding three-centred MOs leading to the **three-centred four-electrons (3c-4e)** bonding system. It seen that the donor pair is stabilized by ΔE energies which is shown below.



The stability of such 3c-4e bonding depends (based on M.O. diagram of H-bonding) on the electronegativity of terminal donor atom. If the terminal donor atom is highly electronegative in nature, then it will give maximum stability of such H-bonding than lower electronegative donor atom. So, higher the magnitude of electronegativity higher will be the strength of H-bonding generally. For this reason, the stability of HF_2^- is maximum than HCl_2^- or HBr_2^- .

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- Comparison between intramolecular and intermolecular H-bonding:

Intramolecular H-bonding	Intermolecular H-bonding
<p>i. H-bonding involve in the same molecule.</p> <p>ii. It lead to chelation (monomeric nature), which leads to decreases the m.p or b.p. of the molecule.</p> <p>iii. Dilution has no effect on intra molecular H-bonding.</p> <p>iv. Its strength is not so high like intermolecular H-bonding.</p>	<p>i. It is formed among the two species of same or different kinds of molecule.</p> <p>ii. It lead to molecular association and there by increases molecular weight of H-bonded species, which leads to increased m.p or b.p. of the molecule.</p> <p>iii. It is concentration dependent. On dilution extend of such intermolecular interaction gradually decreases.</p> <p>iv. Its strength is relatively high.</p>

- Another type of Hydrogen bonding:

Another two types of interesting H-bonding are:

i. Symmetrical H-bonding.

ii. Asymmetrical (unsymmetrical) H-bonding.

Tropic	Symmetrical H-bonding	Asymmetrical H-bonding
Definition:	<p>'H' atom lies on mid-way of X and D (donor) atoms; i.e. equal distance apart from X and D.</p> $\begin{array}{c} r_1 \quad r_2 \\ X \text{---} \text{H} \text{---} D \\ r_1 = r_2 \end{array}$	<p>The distance between 'H' atom with that of X and D (donor) atom is not equal.</p> $\begin{array}{c} r_1 \quad r_2 \\ X \text{---} \text{H} \text{---} D \\ r_1 \neq r_2 \quad r_2 > r_1 \end{array}$
Relative bond energy:	Its H-bond strength greater than unsymmetrical type.	Its H-bond strength lower than symmetrical type.
Stability:	Stability is higher than unsymmetrical type.	Stability is lower than symmetrical type.

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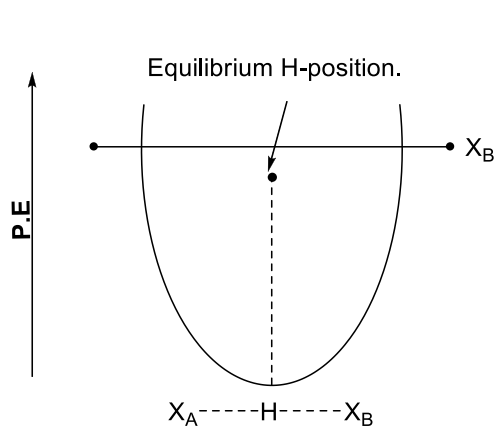
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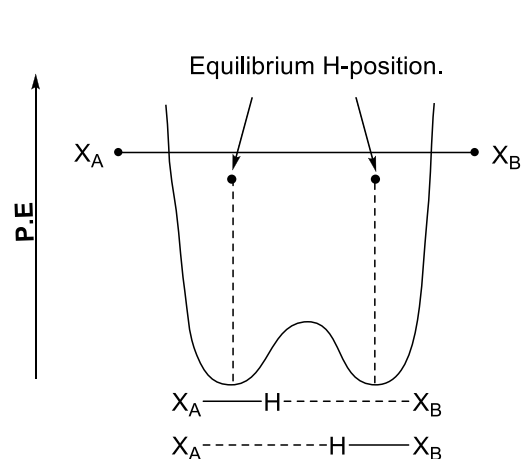
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Potential energy graph:	Its Potential energy graph 'U'-shaped	Its Potential energy graph 'W'-shaped
Nature:	It has linear in nature	It may be linear or non-linear nature
Example:	$[F \cdots H \cdots F]^-$ in HF_2^-	$[Cl-H \cdots Cl]^-$ in HCl_2^-

Potential energy graph of symmetrical and unsymmetrical H-bonding:



P.E Curve for symmetrical H-bonding

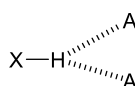


P.E Curve for unsymmetrical H-bonding

- Some other modern (classical) H-bonding:

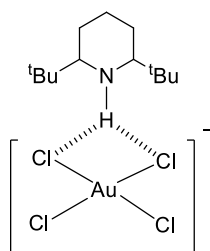
(a) Bifurcated H-bonding:

This type of H-bonding attributed, when a hydrogen atom attached with a electronegative atom and operating weak electrostatic interaction with other two electronegative atoms.



A = Electronegative atom.

e.g.



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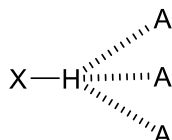
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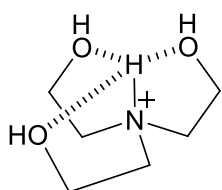
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(b) Trifurcated H-bonding:

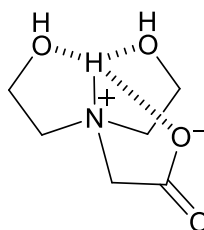
This type of H-bonding attributed, when a hydrogen atom attached with a electronegative atom and operating weak electrostatic interaction with other three electronegative atoms.



e.g.



and



Questions:

1. Alcohol has higher boiling points than those of alkane and ether of comparable molecular weight. – Explain.
2. The *ortho*-compounds may be separated from their *meta* and *para*-isomer by steam distillation. – Explain.
3. Explain why *ortho*-nitrophenol and *ortho*-hydroxybenzaldehyde have much lower boiling point and much lower water solubility than their *meta*- and *para*-isomers.

❖ Application of H-bonding:

1. Melting and boiling point
2. Latent heat of vaporisation
3. Viscosity, surface tension
4. Concentration
5. Solubility
6. Vander Waals constant – a
7. Acid strength
8. Enol content
9. Dehydration of hydrated salt
10. Clathrates cage compound formation

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- Effect on boiling point and melting point:

****Boiling point variation in hydrides of main group elements:**

The intramolecular weaker van der Waals forces (dispersion forces) generally increase with the increase of molecular size and molecular weight and these leads to increase (when hydrogen bonding is expected to be absent then van der Waals forces should be considered) the boiling point of the system generally than lower molecular weight containing systems. But if intermolecular hydrogen bonding present (if electronegativity of central atom is sufficiently higher) then the extend of molecular associations will much higher than that in weak Vander Waals forces (London dispersion forces) leading to increase the boiling point more because of increased in effective molecular weight of such intermolecular H-bonded systems.

- ✚ **B.P. order of Gr. 15 hydrides:** NH_3 (extensive intermolecular hydrogen bonding) \gg $\text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$ (van der Waals forces increases with increasing molecular weight).
- ✚ **B.P order of Group 16 hydrides:** H_2O (extensive intermolecular hydrogen bonding) \gg $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$ (van der Waals forces increases with increasing molecular weight).
- ✚ **B.P. order of Group 17 hydrides:** HF (extensive intermolecular hydrogen bonding) \gg $\text{HCl} < \text{HBr} < \text{HI}$ (van der Waals forces increases with increasing molecular weight).
- ✚ **B.P. order of Gr. 14 hydrides (No hydrogen bonding present here due to insufficient electronegativity of the central atoms):**
 $\text{CH}_4 < \text{SiH}_4 < \text{GeH}_4 < \text{SnH}_4$ (only weaker dispersion forces operating: van der Waals forces increases with increasing molecular weight).
- ✚ but $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$. (No hydrogen bonding only dispersion forces which depend on molecular weight)

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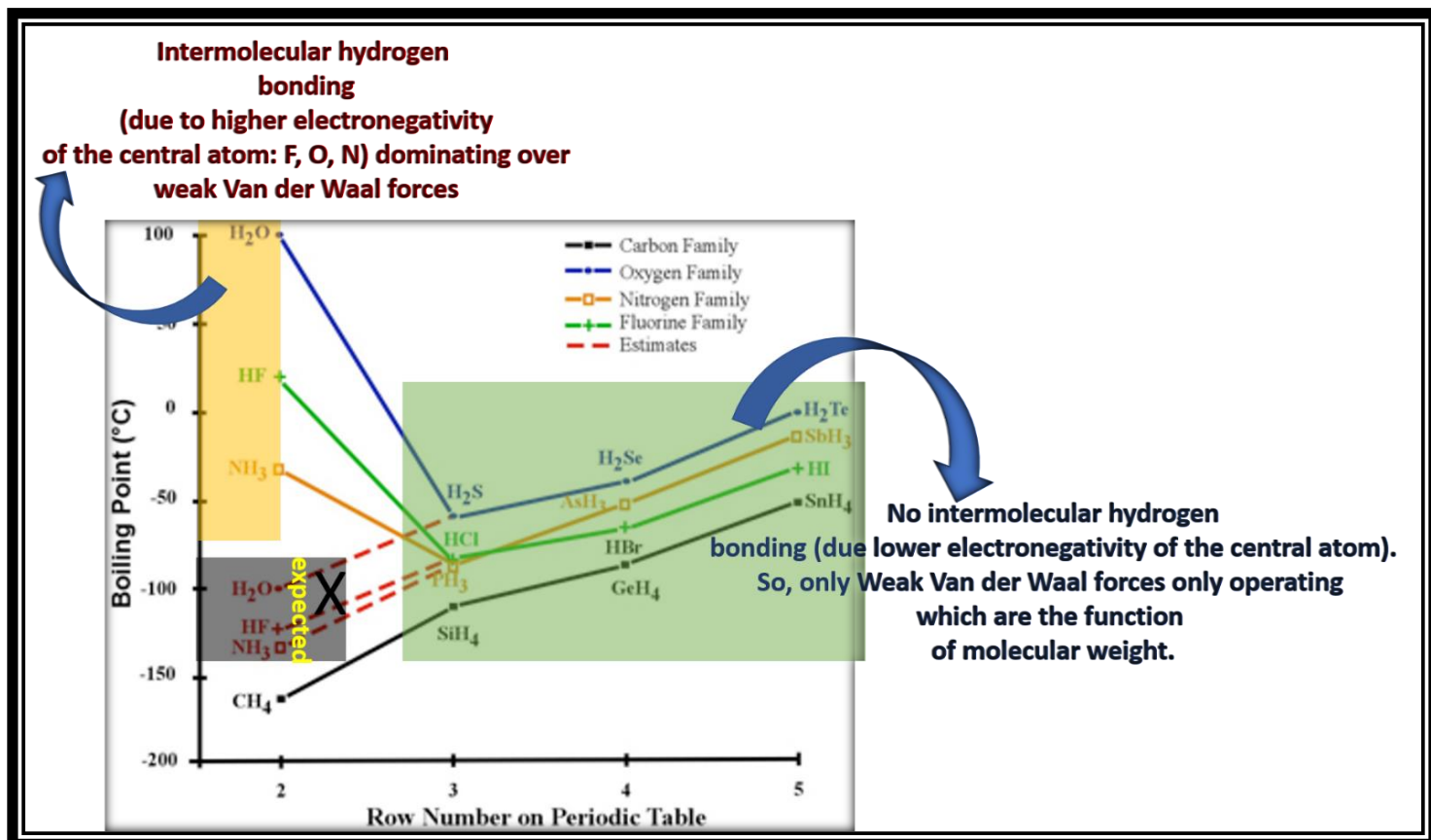
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- **Explanation of abnormally higher boiling point of H₂O (100 °C) than HF (19.6 °C) although the electronegativity of F is higher than O:

Although the electronegativity of F is higher than O but higher boiling point of H₂O (100 °C) is higher than HF (19.6 °C). One water molecule can form four intermolecular H-bonding for which its effective molecular weight is relatively higher while the one HF molecule can form only two such intermolecular H-bonding for which its effective molecular weight is relatively lower than water.

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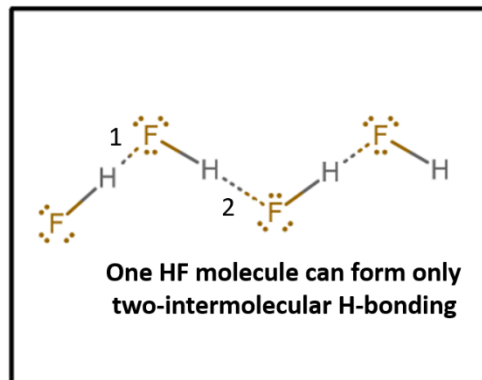
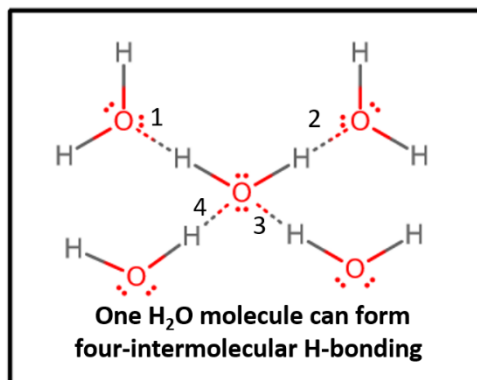
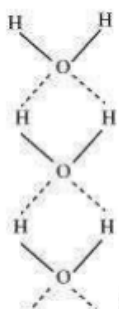
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Besides that, Crystalline HF is polymeric with a planar zigzag chain structure which has lower dipole moment than the chain structure of H₂O molecule.

So, high amount of energy is necessary to break the H-bonding in water molecules than HF. Hence boiling point of H₂O is higher than HF.

✚ Boiling point variation between thiol and alcohol and ethers:

Sulfur is much less electronegative than oxygen, giving S-H bonds a much smaller ionic than O-H bonds. Accordingly, thiols form only very weak hydrogen bonds. As a result, sulphur containing compound have lower boiling point than oxygen analogues, such type of example are shown below.

Oxygen analogues	Boiling point (°C)	Sulfur analogues	Boiling point (°C)
HOH	100	HSH	-62
CH ₃ OH	66	CH ₃ SH	6
CH ₃ COOH	119	CH ₃ COSH	93

✚

But in few cases, Sulphur compounds, owing to larger molecular weights, ordinarily have higher boiling points than the oxygen compounds, examples are shown below;

Oxygen analogues	Boiling point (°C)	Sulfur analogues	Boiling point(°C)
CH ₃ OCH ₃	-24	CH ₃ SCH ₃	38
C ₂ H ₅ OC ₂ H ₅	35	C ₂ H ₅ SC ₂ H ₅	92

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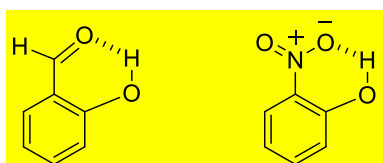
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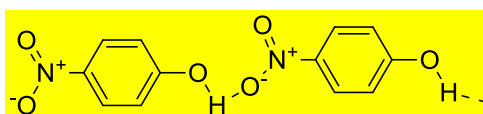
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✚ **Explanation of boiling point and steam volatility in phenolic compounds as well as other systems:

In the case of *ortho*-isomers, molecular association of the -OH group in these molecules is diminished due to chelation (via six member H-bonded cyclic ring formation) with the adjacent carbonyl or nitro group via intramolecular hydrogen bonding [where no molecular association : (monomeric nature)]

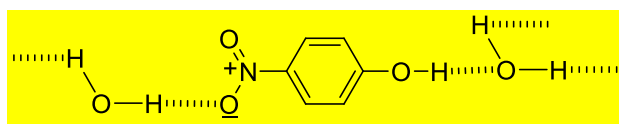


Consequently, the *ortho*-isomer are only sparingly water soluble and much more volatile than the *para*-isomer where intermolecular hydrogen bonding increases the molecular association or aggregation (effective molecular weight increases). Hence hydrogen bonded (intermolecular) molecule will have higher boiling point.



A compound possessing an appreciable vapour pressure at the boiling point of water can be steam-distilled. Because of intramolecular H-bonding, the *ortho*-compounds are boiled at low temperature and they have appreciable vapour pressure at 100°C. But in case of *meta* and *para*-isomer forming intermolecular H-bonding which can increase the effective molecular weight, therefore these isomer are boiled at higher temperature. Consequently *ortho*-compounds can be easily separated from their *meta* and *para*-isomer by steam distillation.

Due to presence of intramolecular H-bonding, the *ortho*-isomer can't form H-bonds with water molecule and hence it is less soluble in water. But in case of *meta*- and *para*-isomer can't form such type intramolecular H-bond, so they can form H-bond with water. Consequently, *meta*- and *para*-isomer are more soluble in water.



para-nitrophenol

As a result of chelation *ortho* and *para*-hydroxy carbonyl or nitro compound are separated by steam distillation.

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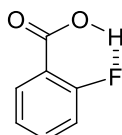
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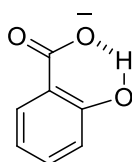
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Similarly, *meta* and *para*-fluorobenzoic acid are much more associated in solution than the *ortho*-fluorobenzoic acid. In this case the *ortho*-fluoro atom ties up the hydroxyl group through chelation which is not possible in *meta* and *para*-isomers.



ortho-fluorobenzoic acid

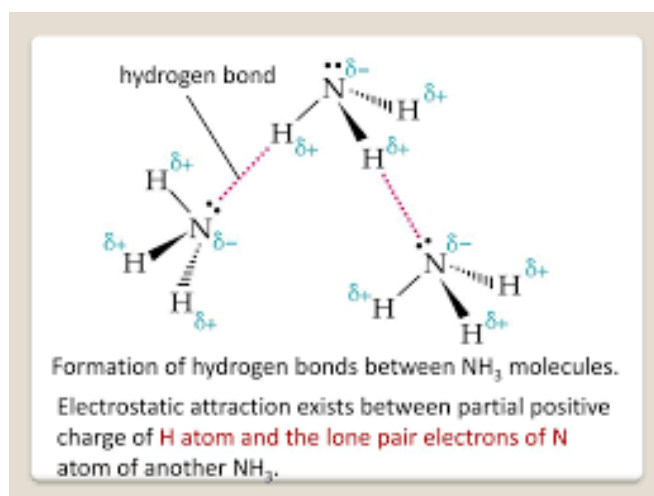
When anion of an acid is stabilised intramolecular H-bonding there is marked increase in the **dissociation of the acid**, such as salicylic acid.



ortho-salicylate

The reciprocal H-bonding between the $-OH$ group of hydroxylic compounds and water markedly increase the water solubility of the hydroxylic compound. When a compound has large ratio of $-OH$ group to hydrocarbon groups, the compound will have significant solubility in water. For example, sugars and certain starches are very soluble in water, and even polyvinyl alcohol, a polymer of large molecular weight is quite soluble in water.

***NH₃ is liquid (three N-H bonds for intermolecular H-bonding) but Me₃N is volatile (no N-H bonds for intermolecular H-bonding).**



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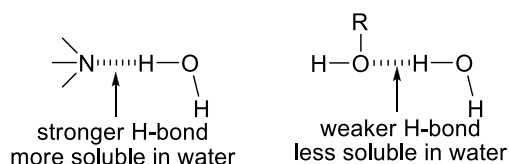
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NH_3 has higher Van der Waal constant 'a', than that of N_2 (a = Vander Waals const.) 'a' originates from the intermolecular force of attraction among the gas molecules. There is higher force of attraction among the NH_3 gas molecules by intermolecular H-bonding. So NH_3 has larger 'a', than that of N_2 .

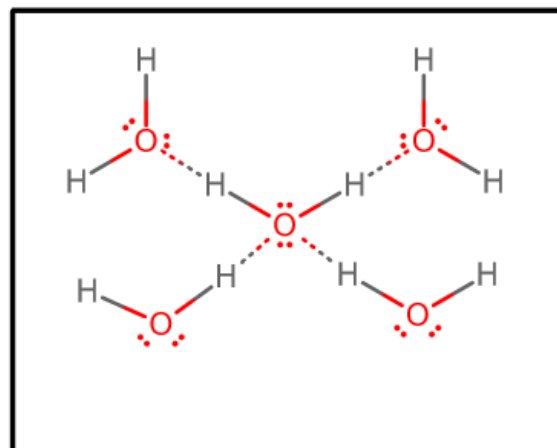
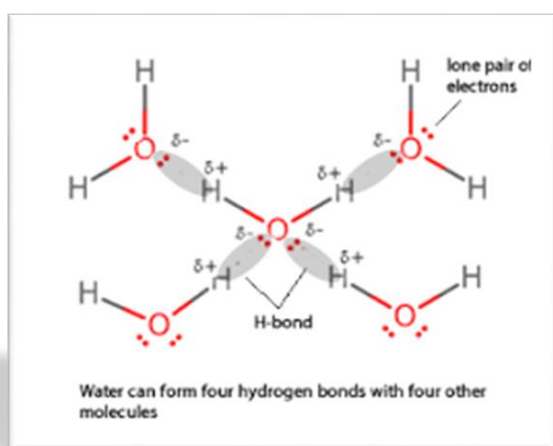
✚ Explanation of solubility between alcohol and amines:

Solubility of alcohol and amine are depending on the strength of intermolecular H-bonding with water molecule. In case of amines forms stronger intermolecular H-bond with water than that of alcohols because nitrogen atom of amines is better hydrogen acceptor (base) than oxygen atom in alcohol. Due to stronger H-bond formation, amines is more water soluble than alcohol.



✚ Explanation of physical state:

- **H_2O liquid, H_2S gas:** In H_2O , many molecules are associated by intermolecular H-bonding (due to high electronegative value and smaller size of oxygen). and attractive force among the H_2O molecules is high so exist as liquid but in H_2S , no intermolecular H-bonding occur due to low electronegative value and larger size and hence it is mainly gas in nature.



For the same reason the boiling point of water is higher (as effective molecular weight in water is higher due to intermolecular H-bonding which gives molecular associations among the water molecules) than H_2S (where no such H-bonding present due to lower electronegativity of S).

HYDROGEN BONDING AND WEAK INTERMOLECULAR FORCES

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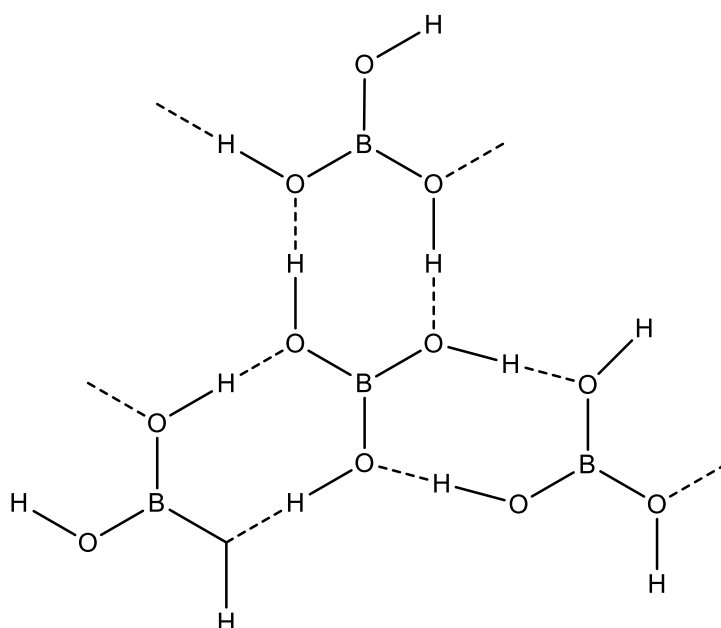
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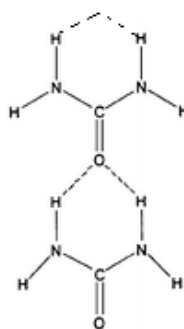
✚ ****Boric acid $B(OH)_3$: H_3BO_3 is solid and soapy to touch and less soluble in water:
Chemistry of boric acid:**

In H_3BO_3 , extensive intermolecular hydrogen bonding occurs among the molecules leading to increase effective molecular weight of the system and form a chain structure (planar sheets of planar trigonal networking) which is two dimensional in nature. So, it exists as a solid with lower solubility because of the higher effective molecular weight.



The adjacent layers in the crystal of boric acid are held together by weak forces of attraction through intermolecular hydrogen bonding. Because of weak forces of attraction, one layer can slide over the other. This makes boric acid soft and Soapy to touch (slightly oily feeling).

- **Urea is solid:** Due to intramolecular H-bonding which makes molecular association and increase the effective molecular weight.



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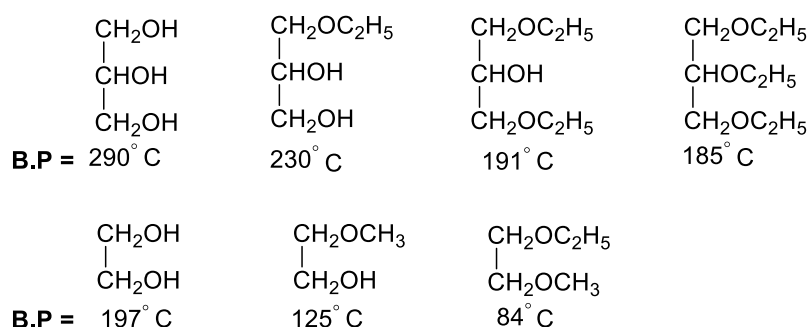
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✚ Effect on H-bonding on physical properties:

Transition Temperature:

Another illustration of the effect of intermolecular hydrogen bonding on boiling points is found in a comparison of the boiling points of polyhydroxy alcohol and their ethers.



As the -OH group successively covered by alkyl groups to block hydrogen bonding, the boiling point progressively decrease in spite of the increase in molecular weights.

The effect of intramolecular H-hydrogen bonding on transition temperature is opposite to that of intermolecular H-bonding.

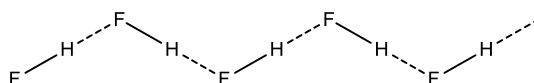
For illustration, the *ortho*- isomer of hydroxy nitro and carbonyl compounds have lower melting point than the *meta* or *para*-isomers (already discussed). In this case, chelation ties up the *ortho* -OH groups and prevents association from occurring, which would otherwise raise the melting points.

Similarly boiling points also decreases for the compounds undergoing chelation via intramolecular hydrogen bonding.

Compound	M.P of <i>ortho</i> -isomer (°C)	M.P of <i>para</i> -isomer (°C)
Nitrophenol	44	114
Nitrobenzoic acid	144	241
Nitrobenzaldehyde	44	106
Dihydroxy benzene	104	169

[Boiling point HF > MeF :

- In HF, solid, liquid and gaseous form contain intermolecular H-bonding.



[Zigzag chain structure of crystalline HF]

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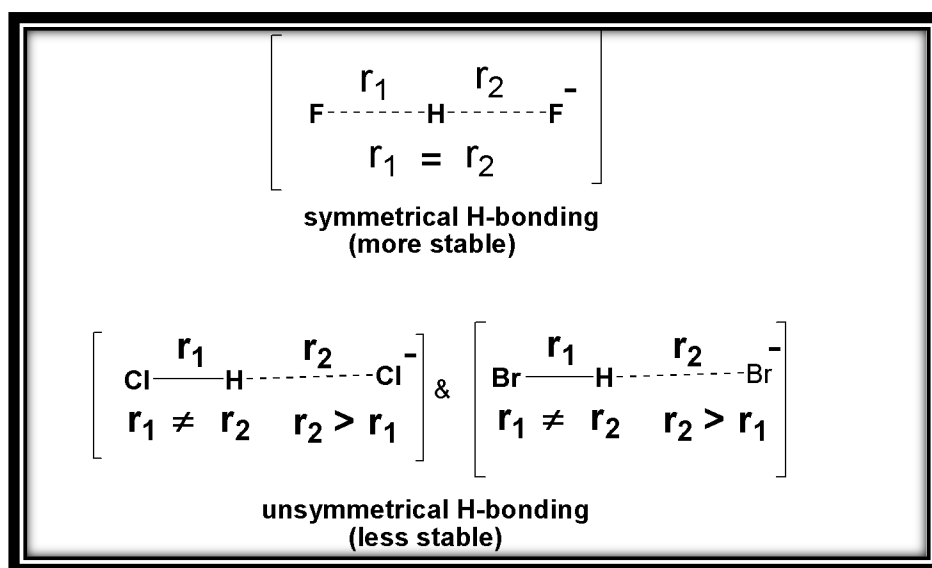
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🚧 Prediction of stability:

****KHF₂ is exist in nature but KHCl₂ and KBr₂ does not exist in nature.**

Reasons:

- (i) The stability of such 3c-4e bonding depends (based on M.O. diagram of H-bonding) on the electronegativity of terminal donor atom. If the terminal donor atom is highly electronegative in nature, then it will give maximum stability of such H-bonding than lower electronegative donor atoms.
- (ii) * In case of HF₂⁻ symmetrical type stable hydrogen bonding present due to higher electronegativity of 'F' but for HCl₂⁻ & HBr₂⁻ unsymmetrical type less stable H-bonding present due to larger size and lower electronegativity of Cl & Br.



- (iii) Anionic radii of HF₂⁻ is comparable with the cationic radii of K⁺ for which the lattice energy of KHF₂ is higher (r₋ ≈ r₊). whereas due to higher size of Cl & Br, the ionic radii of HCl₂⁻ & HBr₂⁻ is relatively higher than the ionic radii of K⁺ (r₋ ≠ r₊). for which the lattice energy of KHCl₂ and KBr₂ are extremely low.

Hence, KHF₂ is exist in nature as a stable salt but KHCl₂ and KBr₂ does not exist in nature.

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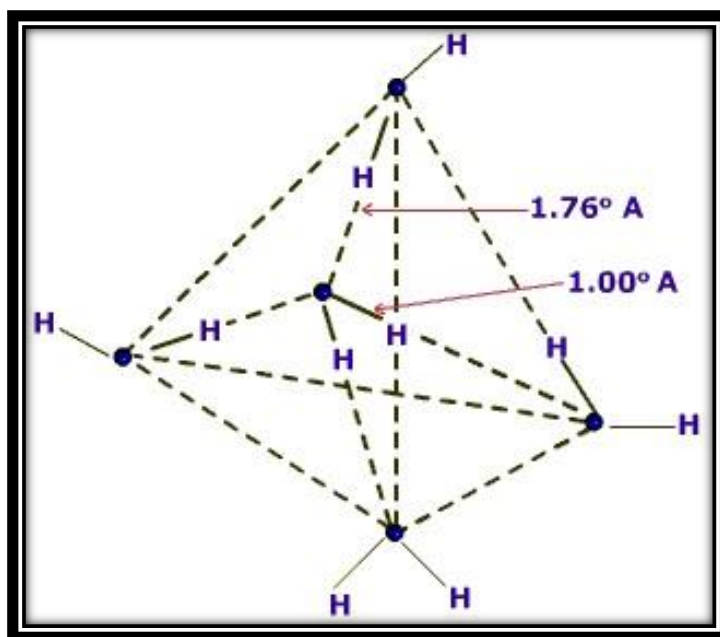
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****Abnormal properties of ice: The density of water is maximum at 4°C: Floating nature of ice:**

- Ice has a lower density than that of water.
- The density of water is maximum at 4°C.

In ice, each oxygen is tetrahedrally surrounded by four hydrogens: -two hydrogens are covalently bonded and other two H-bonded hydrogens from two different adjacent molecules.



there is some void space in this Td-structure and because of this fact, its density is lower than that of liquid water in which H₂O molecules are closely packed. Due to its lower density at 0°C temp ice can float in water.

On increasing the temperature from 0°C, the H-bonded crystal structure starts to break down. Actually, when ice melts, some of these hydrogen bonds break, the water molecules can now come closer. This contraction of volume increases the density of water rather than ice (temp: 0°C to 4°C). But increases in temperature (greater than 4°C), the kinetic energy (K.E.) of the system increases causing thermal expansion as usual. So, two opposing factors, volume contraction and expansion by thermal agitation. Up to 4°C the first factor is prominent and after 4°C the second factor is prominent and hence, the density of water is maximum at 4°C.

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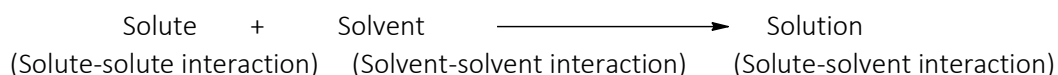
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- Solubility of high molecular weight sugar molecules etc:



If solute-solvent interaction is better than the two possibilities (solute-solute, solvent-solvent interaction) then the solubility is favoured.

- ✚ Glucose, sucrose has many no. of -OH group which form intermolecular hydrogen bonds with water molecule and soluble in H_2O .
- ✚ Benzene, toluene, CCl_4 etc. which can't participate in hydrogen bonding so not soluble in H_2O .
- ✚ Higher members of homologous series such as alcohols, fatty acids and ketones etc. are not soluble in H_2O because of large non-polar hydrophobic moieties in such compounds.
- ✚ Alcohols of lower molecular weight are more soluble in H_2O than the alcohol of higher molecular weight.

✚ *Solubility comparison between:

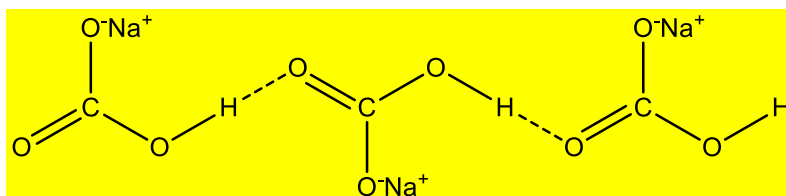
(a) NaHCO_3 Vs. Na_2CO_3

(b) NaHCO_3 Vs. KHCO_3

[**Ans. (a) Na_2CO_3 is more soluble in H_2O than NaHCO_3

(b) KHCO_3 is more soluble in H_2O than NaHCO_3]

NaHCO_3 exists by intermolecular H-bonding among the molecules as follows:



So, its effective molecular weight for this polymeric H-bonded network is higher. Hence it has lower tendency to form intermolecular H-bonding with H_2O and hence less soluble in water. But Na_2CO_3 has more tendency to form H-bonding with H_2O as there is no intermolecular H-bonding among the molecules.

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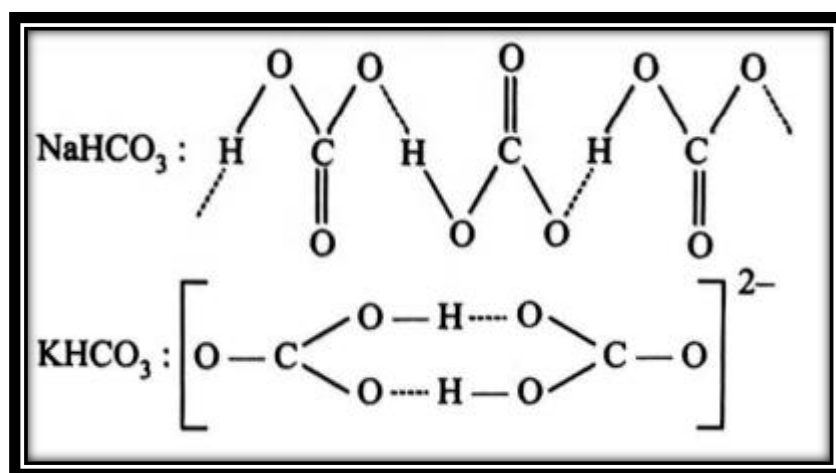
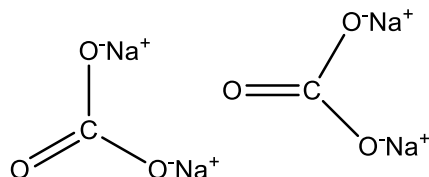
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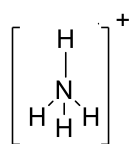
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KHCO₃ can form dimer nature by the given type hydrogen bonding where the effective molecular weight is relatively lower than the polymeric NaHCO₃ (H-bonding given already) for which KHCO₃ is more soluble in water than NaHCO₃.

- NH₄Cl is more soluble in H₂O than that of NaCl.



In NH₄⁺ four N-H bonds are available for intermolecular h-bonding with h₂o. Not only that it has lower lattice energy due to quite larger size of nh₄⁺ for which its hydration energy is higher. NaCl is soluble in h₂o by weak ion-dipole attraction with H₂O molecules and here lattice energy is little higher than nh₄cl too.

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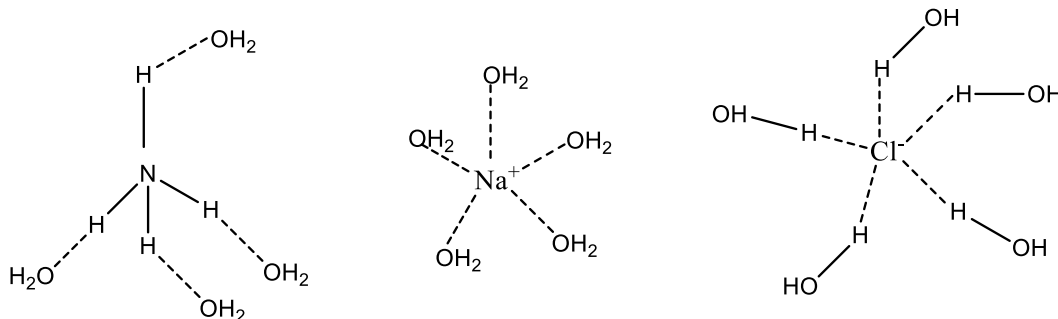
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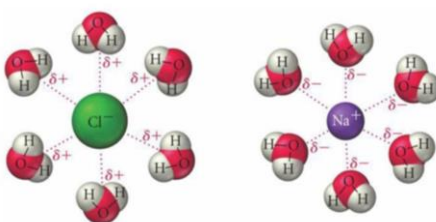
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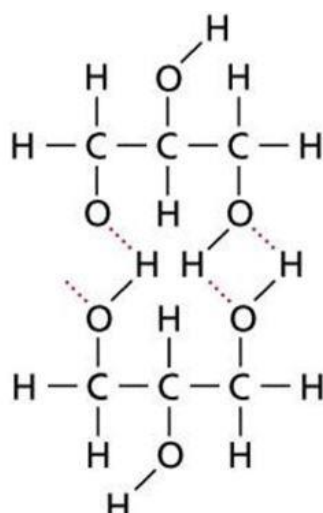
Ion-Dipole Forces



✚ Explanation of Viscosity (dense nature):

Intermolecular H-bonding enhances the intermolecular attraction among the molecules so viscosity increases.

Glycerol has three –OH group for intermolecular H-bonding among the molecules but ethanol has one –OH group for the same. So glycerol is more viscous than ethanol.



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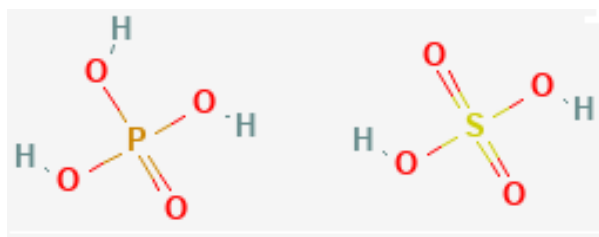
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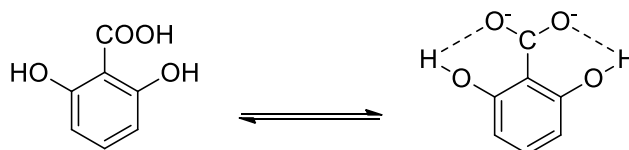
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H_3PO_3 is denser and more viscous than H_2SO_4 . This is due to the fact that H_3PO_3 has three –OH group and H_2SO_4 has two –OH group. Hence the extent of intermolecular hydrogen bonding is higher as well as molecular association in case of H_3PO_3 relative to H_2SO_4 .



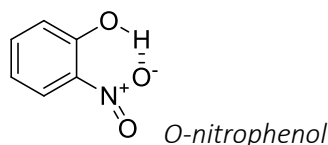
Explanations of Acidity:

- ✓ 2, 6 dihydroxy benzoic acid is more acidic than benzoic acid, as conjugate base of 2, 6 dihydroxy benzoic acid is stabilised by intramolecular H-bonding.



Stabilised by intramolecular H-bonding

- ✓ *o*-nitrophenol is less acidic than *p*-nitrophenol, as –OH group of *o*-nitrophenol is not free due to intramolecular H-bonding between –OH and –NO₂ group (close proximity).



o-nitrophenol

- ✓ Dielectric constant and surface tension increases if intermolecular H-bonding among the molecules is higher.

• **HF is weak monobasic acid but it produces acidic salt:

HF dissociate into water slowly giving F⁻ ion and H⁺ and behave like a weak mono basic acid but it itself acting as a fluoride ion (F⁻) acceptor giving rise to stable HF₂⁻ salt formation where symmetrical type H-bonding present and this lead to shift the equilibrium into right hand side with slight increase in the concentration of H₃O⁺ for which its salt behave like a acidic salt.

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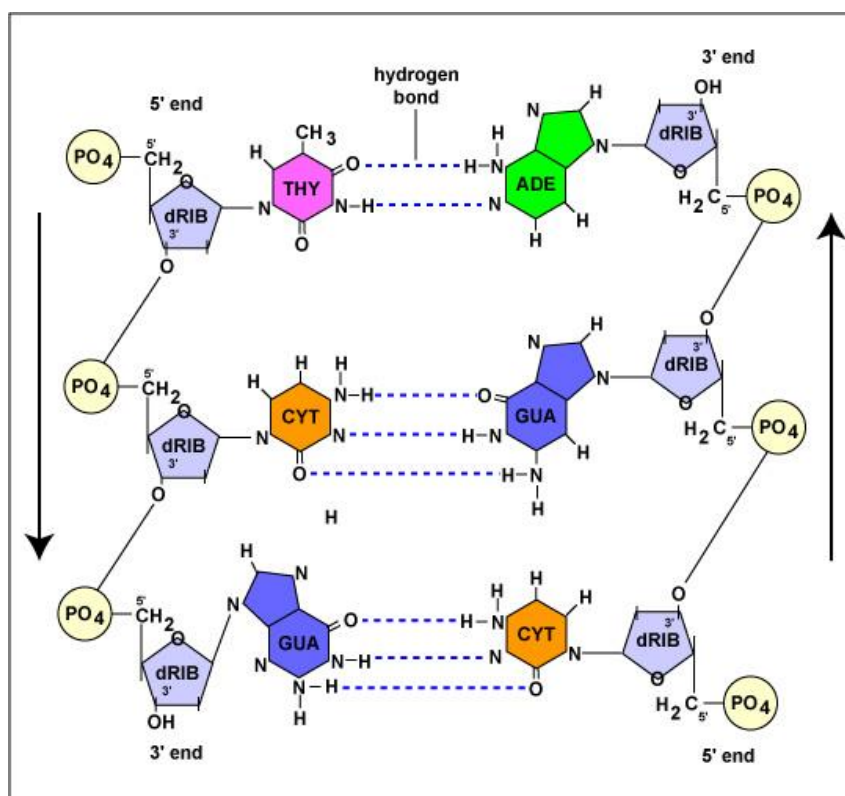
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- Importance of H-bond in Biological System :

Proteins contain chains of amino acids by hydrogen bond. The amino acid units are arranged in a spiral form, somewhat like a stretched coil spring (forming a helix). The N-H group of each amino acid unit and the fourth C=O group following it along the chain establishes NH---O hydrogen bonds. These bonds are partly responsible for the stability of the spiral structure. Nucleic acids also contain extensive hydrogen bonding.

DNA consists of two intertwining helices (a double helix) held together by hydrogen bonding.



H-bonding gives extra stability in DNA.

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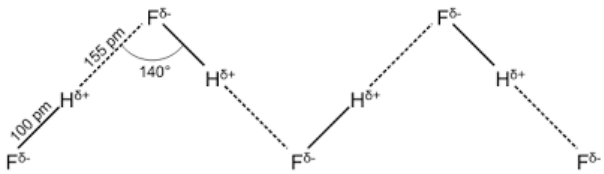
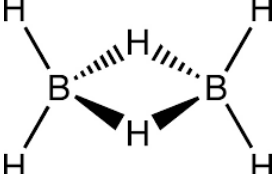
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- ❖ H-bonding Vs H-bridging bonding:

H- bonding	H-bridging bonding
Special type of dipole-dipole interaction where two atoms (non-metallic containing one H-atom) must have different electronegativity (one having very higher electronegative: F, O, N)	It is bridging (banana type) bonding where electronegativity between two atoms has almost similar (but one of the atoms must be electron deficient and have a scope for co-valency expansion)
3c-4e type bonding M.O.	3c-2e type bonding M.O.
 <p>Found in HF and water etc</p>	 <p>Found in diborane (B₂H₆)</p>



Other weaker Intermolecular forces

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Intermolecular Forces

Intermolecular Forces	Formed by the attraction between ...	Examples
Ion-dipole	an ion and a polar molecule	Na ⁺ and H ₂ O
Hydrogen bond	molecules which have H on N, O, or F atoms	H ₂ O and H ₂ O; H ₂ O and CH ₃ CH ₂ OH
Dipole - Dipole	two polar molecules	CH ₃ Br and ICl; CH ₃ Br and H ₂ O
Ion - Induced dipole	an ion and a nonpolar	Fe ²⁺ and O ₂
Dipole - Induced dipole	a polar molecule and a nonpolar molecule	HCl and Cl ₂
London (dispersion) forces	two nonpolar molecules	CH ₄ and CH ₄ ; F ₂ and F ₂ ; CH ₄ and F ₂

Strength

IMF	Distance-dependence	Other Factors	Typical Magnitude
Covalent Bonding	$e^{-\alpha r}$		400 kJ mol ⁻¹
Short-range Repulsion	$e^{-\alpha r}$		
Electrostatic			
Ion-Ion	r^{-1}	$Q_1 Q_2$	250 kJ mol ⁻¹
Ion-Dipole	r^{-2}	$Q_1 \mu_2$	15 kJ mol ⁻¹
Dipole-Dipole (static)	r^{-3}	$\mu_1 \mu_2$	2 kJ mol ⁻¹
Dipole-Dipole (rotating)	r^{-6}	$\mu_1 \mu_2$	0.6 kJ mol ⁻¹
Induction			
Ion-Induced Dipole	r^{-4}	$Q_1^2 \alpha_2$	10 kJ mol ⁻¹
Dipole-Induced Dipole	r^{-6}	$\mu_1^2 \alpha_2$	< 1 kJ mol ⁻¹
Dispersion	r^{-6}	$\alpha_1 \alpha_2 (I_1 I_2 / (I_1 + I_2))$	5 kJ mol ⁻¹
Hydrogen Bonding	$e^{-\alpha r}$		20 kJ mol ⁻¹

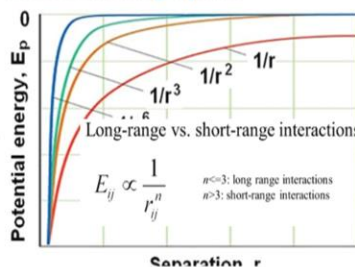
Distance dependence of potential energy of interaction

$1/r$: between ions (ionic bonding)

$1/r^2$: between ions and dipoles

$1/r^3$: between stationary dipoles

$1/r^6$: between rotating dipoles



Type of interaction	Strength	Direction	Range (d)
Coulomb or electric	Very strong	Attractive or repulsive	Medium (1/d ²)
Hydrogen bond	Very strong	Attractive	Long
Steric hindrance	Very strong	Repulsive	Very short
$\pi-\pi$	Strong	Attractive (donor or acceptor) or repulsive	Medium
Ion-dipole	Strong	Attractive	Short
Dipole-dipole	Intermediate	Attractive	Short (1/d ³)
Dipole-induced-dipole	Weak	Attractive (1/d ⁶)	Very short
London dispersion	Very weak	Attractive	Very short (1/d ⁶)

Range of Electrostatic Interactions

Type	Range	Energy (kJ/mol)	Comment
Ion-Ion	1/r	250	
Ion-dipole	1/r ²	15	
Dipole-Dipole	1/r ³	2	Static dipoles (solid phase)
Dipole-quadrupole	1/r ⁴		Fixed Orientation / Linear
Quadrupole-quadrupole	1/r ⁵		Fixed Orientation / Linear

Attraction between neighbouring molecules causes dispersion forces

HYDROGEN BONDING AND WEAK INTERMOLECULAR FORCES

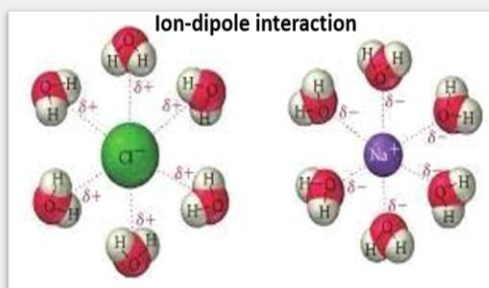
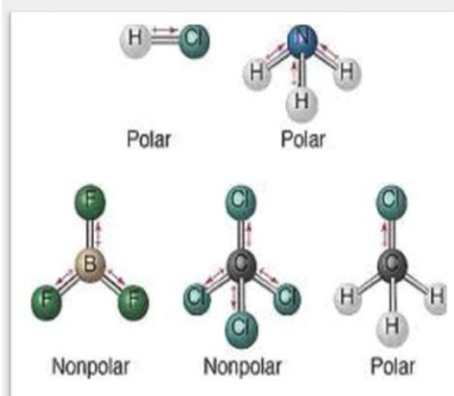
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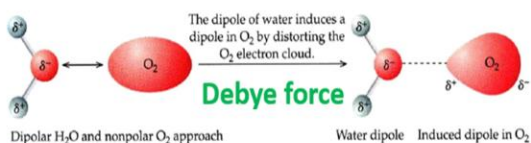
Dipole-dipole

- forces of attraction between oppositely charged ends of **polar molecules**.
- the strength of the dipole-dipole force is dependent on the polarity of the molecule

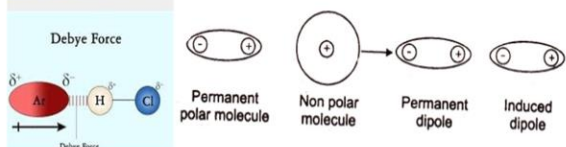


Dipole-induced dipole interactions

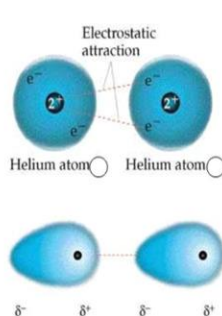
- When a **non-polar** molecule approaches a **polar** molecule (with a permanent dipole), a **dipole** will be induced in the non-polar molecule.



Dispersion forces exist among all molecules and **contribute most** to the overall van der Waals' forces.



London Dispersion Forces (aka van der Waals Forces)



The electrons on one atom are attracted to the nucleus on a neighboring atom.

This creates an "instantaneous" (i.e. temporary) dipole on the first atom.

The instantaneous dipole on the first atom then induces an instantaneous dipole on the second atom.

The two induced dipoles attract each other.

Induced dipole-induced dipole

London Dispersion Forces are proportional to a molecule's polarizability, which is the ease with which the electron cloud can be deformed.

The polarizability, is approximately proportional to the number of electrons in the molecule

Noble gases are non-polar and thus exhibit instantaneous dipole-induced dipole or London forces. Due to these intermolecular forces they are liquefied. An ideal gas having no intermolecular force between its molecules cannot be liquefied by any means.

This tendency to create "temporary dipoles" is called **polarizability**

Polarizability increases with atomic size

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- **Dependent factors for van der Waals forces (weak dispersion forces):**
 - (i) ****They depend on atomic or molecular size as well as atomic or molecular weight (mass), higher the size or weight (mass) higher will be the weaker intermolecular dispersion forces.**
(i.e dispersion force the function of atomic and molecular weight)
 - (ii) With increasing number of valence electrons these forces also increasing.
 - (iii) **** Higher polarizability** (loosely bound outermost electron cloud in lower electronegative systems), higher will be dispersion forces (**London dispersion forces which is directly proportional with the polarizability of the atom/molecule**).
 - (iv) Surface area too.
 - (v) **Dispersion forces may decrease** if $p\pi - p\pi$ or $p\pi - d\pi$ back bonding present as such factor give extra stability in that molecules and so they will not under goes molecular association rather they try to exist as monomeric form.

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❖ Application of dispersion forces:

✓ Prediction of physical state:

➤ (A) * **I₂ is found to be solid.**

London dispersion force (Instantaneous Dipole-Induced Dipole Force) for the **non-polar (zero di moment) I₂** molecule is found to be **higher** than the other lighter members of this group (Gr.-17) due to:

- (i) Larger size and lower electroactivity of **heavier** (higher atomic mass) 'I' atom.
- (ii) Higher **polarizability** of 'I' (presence of loosely bound electron cloud due to lower electronegativity)

I₂ molecules associates together by intermolecular force of attraction via **London dispersion force and so it is solid in nature.**

➤ (B) In BX₃ [X=F, Cl, Br, I] type molecule **BI₃ is solid:**

London dispersion force (Instantaneous Dipole-Induced Dipole Force) for the **non-polar (zero dipole moment due to symmetrical trigonal planar structure) BI₃** molecule is found to be **higher** than the other BX₃ [BF₃ (gas) , BCl₃ (liq.) & BBr₃ (Liq.)] due to:

- (i) Molecular weight of BI₃ is higher than the other BX₃ due to the presence of **heavier** (higher atomic mass) 'I' atom
- (ii) Higher **polarizability** of 'I' (presence of loosely bound electron cloud due to lower electronegativity of 'I')
- (iii) Additionally, the tendency of **p_π(X) → p_π(B) back bonding** gradually decreasing with increasing atomic orbital size of halide (X)
Order of London dispersion forces runs as: BF₃ (gas) < BCl₃ (liq.) < BBr₃ (Liq.) < BI₃ (solid)

Hence to get extra stability BI₃ molecules associates together by intermolecular force of attraction via **London dispersion force and so it is solid in nature.**

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✓ *Prediction of abnormal boiling point:

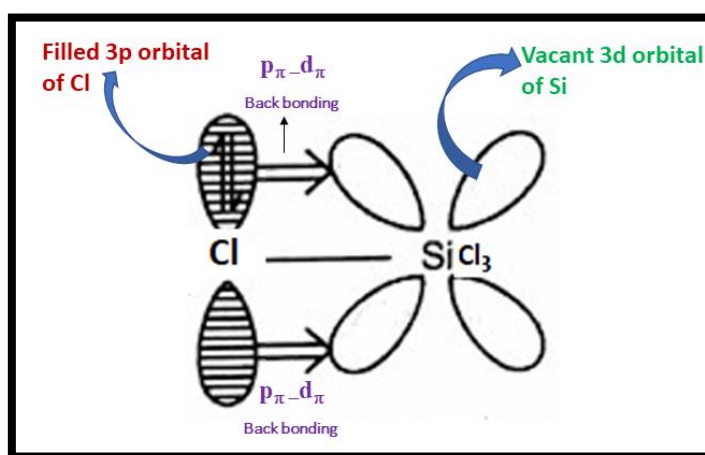
➤ ****Boiling point of SiCl₄ is lower than CCl₄ although the molecular weight of SiCl₄ is higher than CCl₄: SiCl₄ is much volatile than CCl₄**

We know the van der Waals (dispersion) forces are the function of molecular weight; higher the molecular weight of a molecule higher will be the dispersion forces which may leads to molecular association and hence, the boiling point of SiCl₄ should be higher.

But in this case Boiling point of SiCl₄ is lower than CCl₄ although the molecular weight of SiCl₄ is higher than CCl₄. This can be explained the following ways:

Based on $p_{\pi}(\text{Cl}) \longrightarrow d_{\pi}(\text{Si})$ back bonding:

due to presence of suitable vacant 3d orbital in Si, $3p_{\pi}(\text{Cl}) \longrightarrow 3d_{\pi}(\text{Si})$ back bonding gives extra stability in SiCl₄. Hence here dispersion forces are not important for which it does not under goes molecular association. Hence it has low boiling point as here effective molecular weight quite low than CCl₄.



But in case of CCl₄, due to lack of suitable d-orbital in 'C', such $p_{\pi} - d_{\pi}$ back bonding is absent for CCl₄. Hence CCl₄ (non-polar) molecules associates together by intermolecular force of attraction via London dispersion force. So, its boiling point is relatively higher due to higher effective molecular weight.

The periphery of SiCl₄ have higher δ^{-} charge due to higher electronegativity difference [$(\chi^{\text{Cl}} - \chi^{\text{Si}}) > (\chi^{\text{Cl}} - \chi^{\text{C}})$] for which the SiCl₄ molecules repel each other more lowering the dispersion forces and this factor additionally may also decrease boiling point of SiCl₄.

Hence, SiCl₄ is much volatile than CCl₄.

HYDROGEN BONDING AND WEAK INTERMOLECULAR FORCES

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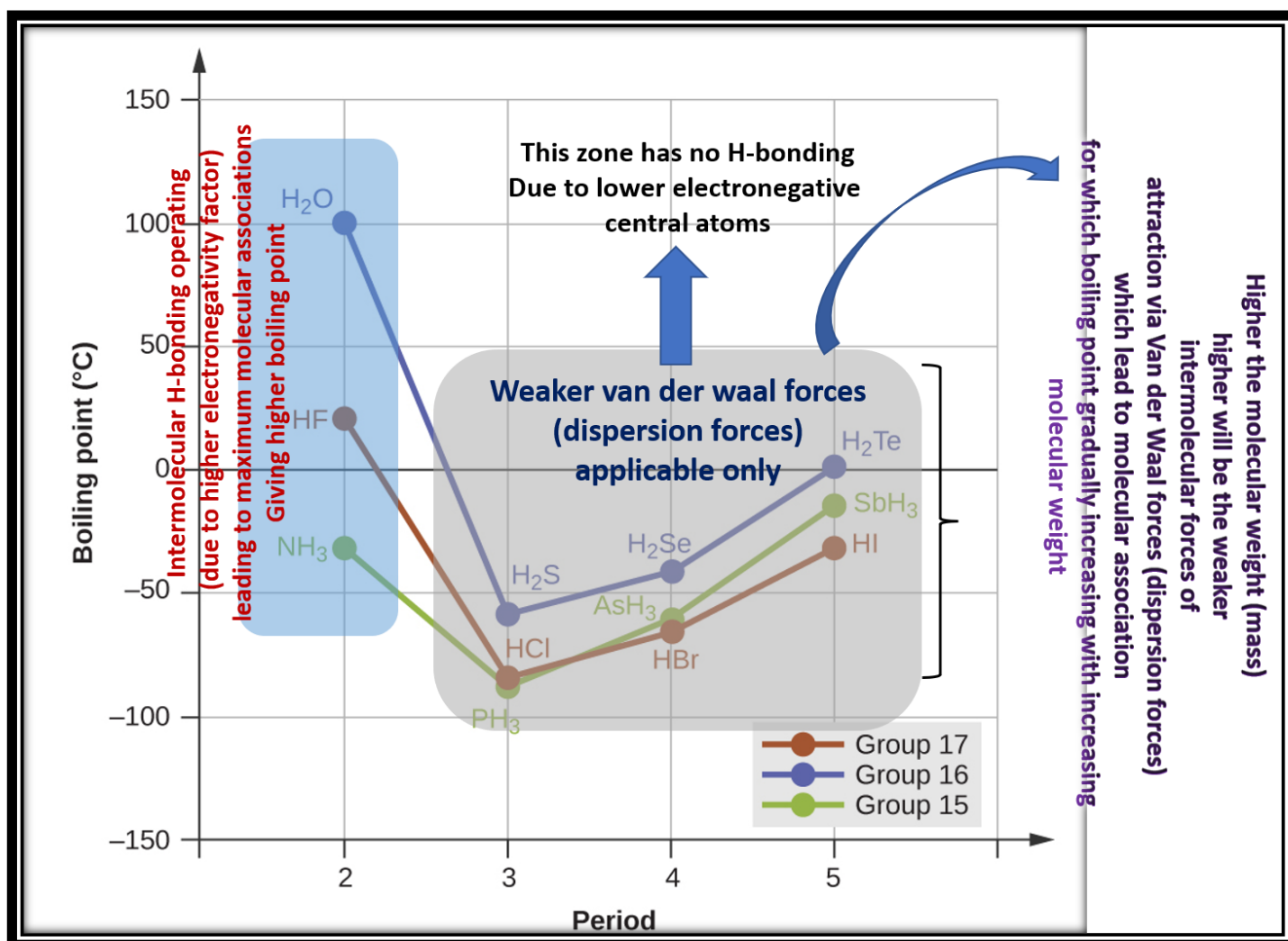
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➤ **** Boiling point variations in hydrides of various groups:**



➤ *** NF₃ has low boiling point than NMe₃:**

This is due to following factors:

- (i) Although both have pyramidal structure but the effective dipole moment in NF₃ is less due to partial cancellation of three resultant N-F ($\chi^F > \chi^N$) bond moment with respect to the bond moment of lone pair as they operate oppositely. But in case of NMe₃ the three N-C ($\chi^N > \chi^C$) bond moments operate in the same direction with the bond moment of lone pair and hence the resultant dipole moment of NMe₃ is higher.

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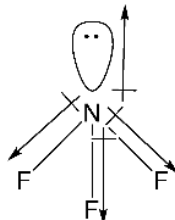
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Hence, NMe_3 is more polar than NF_3 for which dipole-dipole interaction among the NMe_3 molecules is higher than NF_3 which lead to better molecular association for NMe_3 molecules.

- (ii) The molecular weight of NMe_3 is higher than NF_3 . Hence the dispersion forces are higher for NMe_3 than NF_3 . Higher the dispersion forces higher will be the molecular associations among molecules.

Hence, NF_3 has low boiling point than NMe_3 .

- ✓ Formation of Clathrates or Cage compounds of noble gas:

Clathrates are the compounds in which some molecules or atoms (inert gases which are capable of independent existence) are physically trapped in the cavities of the crystal structure of some suitable organic and inorganic compounds.

Example: Crystallization of quinol (1, 4 dihydroxy benzene), **inert gases** (like Ar) are trapped in the cavities by **dipole-induced dipole** supramolecular interaction. He and Xe are not trapped generally due to very small size of He and large size of Xe.

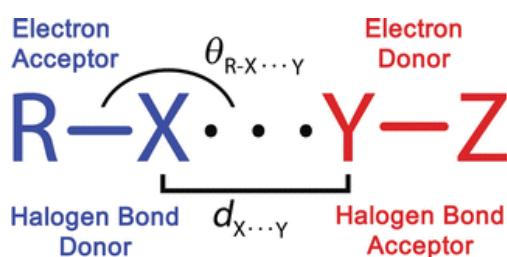
They are not compound, as there is no covalent or ionic bonds i.e.; chemical bonding, they are physically trapped.

❖ Other:

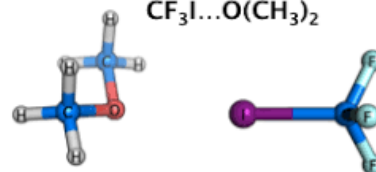
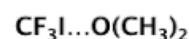
- ✓ Hydrates of Noble gas:

$\text{Kr}(\text{PhOH})_2$ and hydrates of several noble gas compounds are found in nature due to **dipole-induced dipole interaction**.

- ✓ Solubility of ionic lattice is due to ion-dipole interaction.



HALOGEN BONDING



HYDROGEN BONDING AND WEAK INTERMOLECULAR FORCES

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List of: Questions:

1. *Discuss the M.O. of HF_2^- .
2. *Predict the strength of H-bonding in $(\text{FH}\cdots\text{F})$, $(\text{OH}\cdots\text{O})$, $(\text{NH}\cdots\text{N})$.
3. Write down the differences between symmetrical H-bonding and asymmetrical H-bonding.
4. KCl_2 is stable but KClO_2 & KBrO_2 are unstable. Why?
5. ** KClO_2 is found in nature but KClO_2 & KBrO_2 are not. Why?
6. *Arrange the boiling point order of Gr.-15 and Gr.-16 hydrides with reason.
7. **Boiling point of HF is lower than H_2O . Why?
8. H_2O is liquid but H_2S is gas. Explain.
9. *o-nitro phenol is more steam volatile than p-nitro phenol. Explain
10. Boiling point of o-nitro phenol is lower than p-nitro phenol. Explain.
11. * H_3BO_3 is solid and soapy to touch and less soluble in water. Why?
12. *The density of water is maximum at 4°C . Explain.
13. Why ice can float in water?
14. * NaHCO_3 is lower soluble than Na_2CO_3 in water
15. * NaHCO_3 is lower soluble than KHCO_3 in water
16. *Glycerol and H_3PO_4 are denser and viscous. Why?
17. *HF is weak monobasic acid but it produces acidic salt. Explain.
18. *All water molecules in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are not equivalent.
19. Distinguish between H-bonding and H-bridging bonding.
20. * I_2 is found to be solid. Why?
21. *Discuss the physical state of various of various BX_3 (X= F, Cl, Br, I) type molecules.
22. **Boiling point of SiCl_4 is lower than CCl_4 although the molecular weight of SiCl_4 is higher than CCl_4 . Explain.
23. * NF_3 has low boiling point than NMe_3 .
24. Some noble gases form hydrate and clathrate compounds. What are the driving force behind this?