Atomes et molécules

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Chapter 9 : **Weak bonds**

Chapter 9 – Index

Chapter 9 – 1. Weak bonds

A molecule is a set of atoms connected by very stable covalent bonds. (the covalent bond energy is more than 100 de kJ.mol $^{-1}$).

However non covalent molecular interaction also exist:

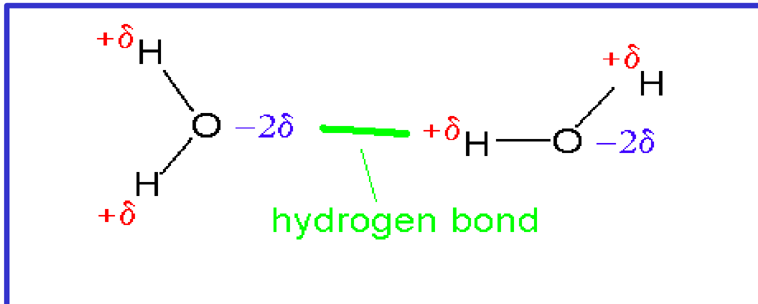
- Different molecules ☞ INTERmolecular interactions

or

- different parts of the same molecule☞ INTRAmolecular interactions

They are called low energy interactions or Non-bonded Interactions (NO NEW MOLECULE)

(< 50 kJ.mol $^{-1}$)



Chapter 9 – 1. Weak bonds

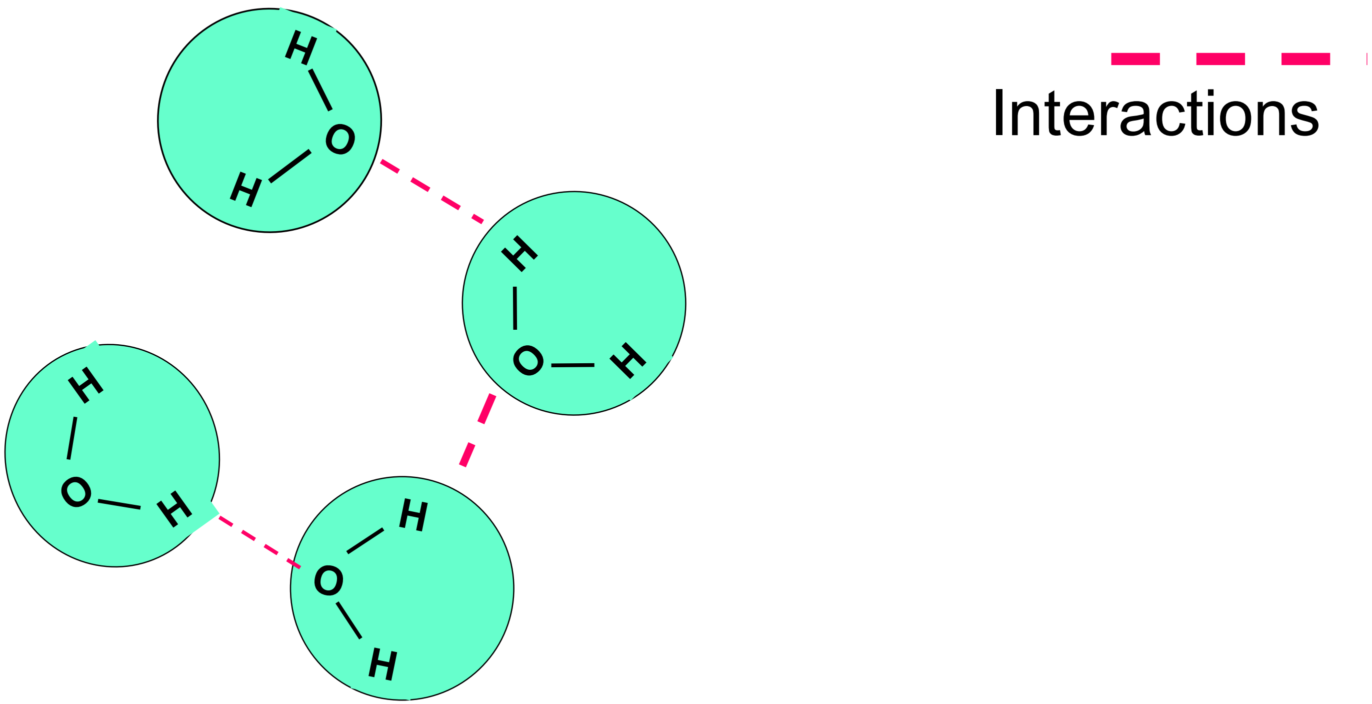
Weak interactions have consequences on:

- **The cohesion of liquids and solids**
- **Physical properties (boiling temperature, solubility in water, and in organic solvants etc…).**
- **Structure of biomolecules (proteines, DNA etc…)**

Those interactions are partly due to the polarization of the molecule.

Chapter 9 – 1. Weak bonds

Example: Intermolecular interaction between water molecules



Those interactions are not covalent. No new molecule are formed. Low energy interactions are the reason why water is liquid at room temperature. Boiling water stops the weak energy interactions but does not break the water molecules. Weak interactions correspond to the cohesion of solids or liquids.

2-1) Definition

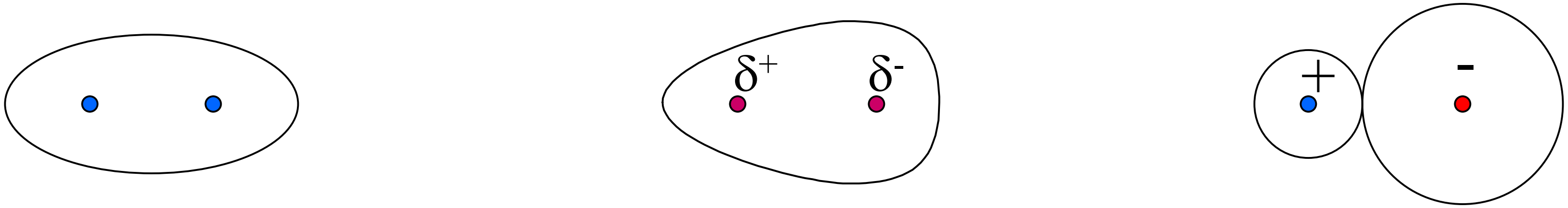
- For a covalent bond between atoms with different electronegativity, the most electronegative atom attracts strongly the bonding pairs
- Because electrons have a negative charge, the unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charges described by $\delta+$ et $\delta-$

$$0 \leq |\delta| \leq 1$$

δ represents the partial ionic character of a bond

Chapter 9 – 2. Polarization

- The molecule has a partial ionic character : the bond is therefore **polarized**



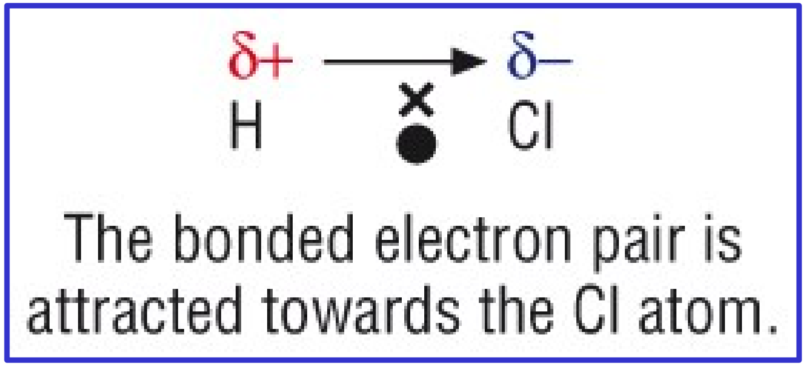
pure covalent bond
δ close to 0

polarised bond
$0 < \delta < 1$

pure ionic bond
$\delta = 1$

Example: HCl (Electronegativities: E-$_{Cl}$ = 3 ; E- $_{H}$ = 2,1)

Chlorine attracts more efficiently negative charges than H.



The bonded electron pair is attracted towards the Cl atom.

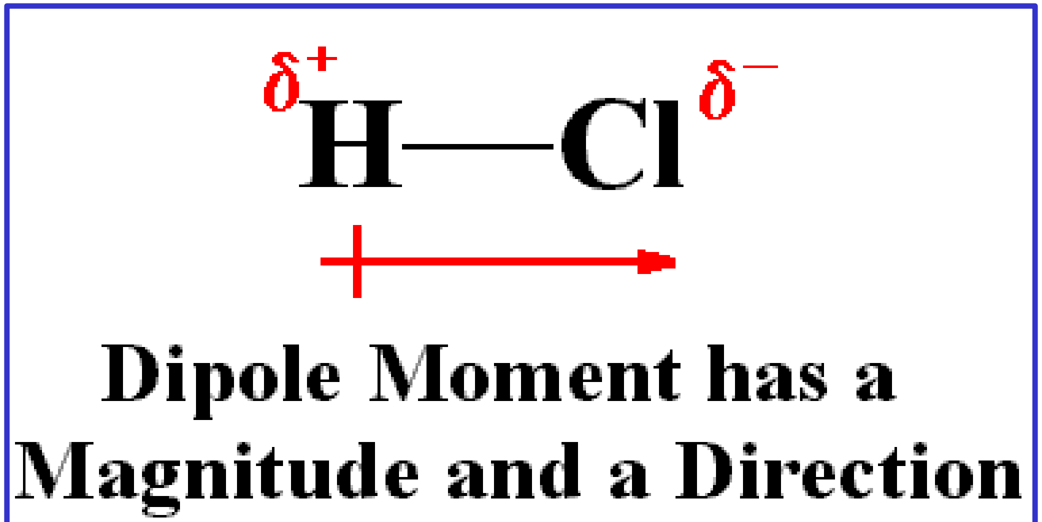
II-2) Dipolar moment

a/ Diatomic molecules

- We say that the HCl molecule has a **permanent dipole**:

Di - ' 2 '
Pole - poles (positive and negative)

- HCl is oriented by an electric field.
- The dipole moment µ is a vector. It is oriented from positive to the negative pole (According to chemists : movement of the elecron attracted by the most electronegative pole !)



Dipole Moment has a Magnitude and a Direction

Chapter 9 – 2. Polarization

For a polarized A – B molecule where B is more electronegative than A:

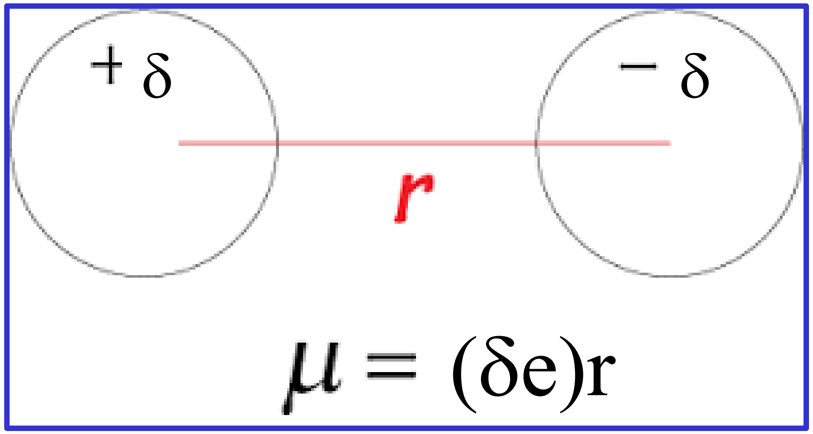
$^{+\delta}\mathbf{A} - \mathbf{B}^{-\delta}$

The dipolar moment µ [expressed in coulomb.metre], is equal to:

δ : partial charge difference $0 \leq |\delta| \leq 1$

e: $1{,}6.10^{-19}$ coulomb

r: interatomic distance[metre]



$$\mu = (\delta e)r$$

Chapter 9 – 2. Polarization

- The product e.δ.r is very small, and the dipolar moment is usually expressed in Debye (D).

$$1\ \mathrm{D} = 3{,}328\ .\ 10^{-30}\ \mathrm{C.m} = 1.6\ 10^{-19}.0.208\ 10^{-10}$$

(electron –proton separated by 0.208 Å)

- The partial ionic character of a molecular bond is equal to experimental dipolar moment μ_{exp} divided by the theoretical dipolar moment $\mu_{A^+\,B^-}$ corresponding to a full ionic bond ($\delta = 1$).

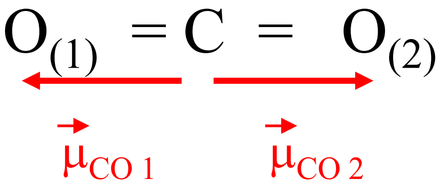
Chapter 9 – 2. Polarization

b/ Polyatomic molecules

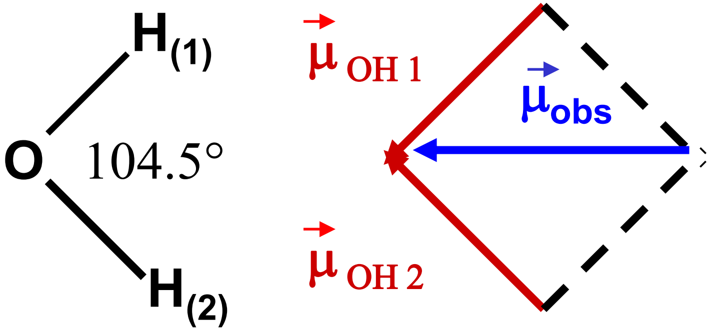
In first approximation, the dipolar moment of a molecule is equal to the sum of dipolar moment of all the bonds.

- The $\vec{\mu}$ must be additioned
- The resulting dipolar moment depends on the molecular geometry

Examples:



$\mu_{CO_2} = 0$



$\mu_{H2O} = 1{,}85$ D

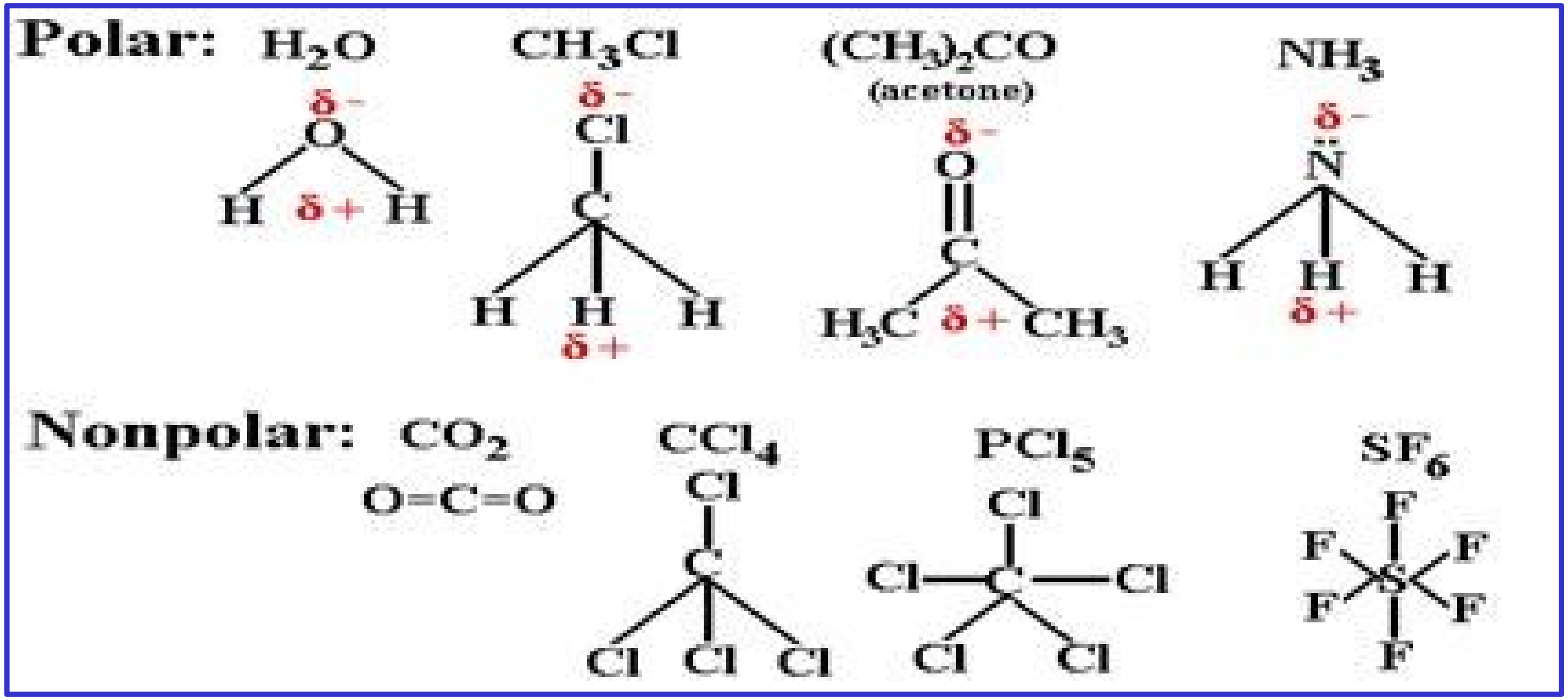
Water has a dipolar moment ≠ 0.
It has a permanent dipolar moment.

Chapter 9 – 2. Polarization

c/ Polar and non polar molecules

- Molecules with a permanent dipol moment ($\mu \neq 0$) are POLAR.

- Molecules with a permanent dipol moment ($\mu = 0$) are NON POLAR.



QCM 18 Sachant que l'atome de fluor F est beaucoup plus électronégatif que l'atome de germanium Ge, quelle(s) est (sont) la (les) proposition(s) exacte(s) :

- **a.** La liaison Ge-F est polarisée $\mathrm{Ge}^{\delta+} - \mathrm{F}^{\delta-}$
- **b.** La liaison Ge-F est polarisée $\mathrm{Ge}^{\delta-} - \mathrm{F}^{\delta+}$
- **c.** La liaison Ge-F n'est pas polarisée
- **d.** Le vecteur moment dipolaire est dirigé de l'atome de germanium vers l'atome de fluor (convention des chimistes)
- **e.** Le vecteur moment dipolaire est dirigé de l'atome de fluor vers l'atome de germanium (convention des chimistes).

QCM 19 On considère la molécule $\underline{\mathrm{C}}\mathrm{O}_2$ ($Z_{\mathrm{C}} = 6$, $Z_{\mathrm{O}} = 8$ et $E^{-}_{C} = 2,5$, $E^{-}_{O} = 3,5$). Quelle(s) est (sont) la (les) proposition(s) exacte(s) :

- **a.** La molécule est en forme de V (géométrie coudée)
- **b.** Les liaisons entre l'atome de carbone et les atomes d'oxygène sont polarisées
- **c.** La molécule est apolaire
- **d.** Le moment dipolaire de cette molécule est voisin de 3 Debye
- **e.** Aucune des propositions ci-dessus n'est exacte.

3-1) VAN DER WAALS interactions

- **Van des Waals interactions are** the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) **other** than those due to **covalent bonds**, or the **electrostatic interaction of ions** with one another, with neutral molecules, or with charged molecules.

Three van der Waals interaction exist:

- force between two **permanent dipoles** (**Keesom force**)
- force between two instantaneously **induced dipoles** (**London dispersion force**). Possible between non polar molecules.

And NOT described in this class:

- force between a permanent dipole and a corresponding induced dipole (**Debye force**).

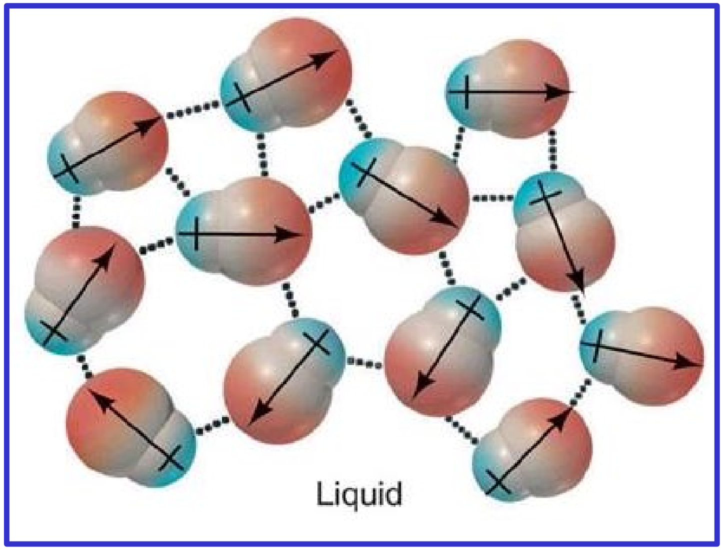
Chapter 9 – 3. Inter and intra-molecular interactions

a/ Interactions between permanent dipoles: KEESOM forces

- **Electrostatic attraction exists between 2 polar molecules (the positive pole of a molecule attracts the negative pole of the other molecule.**

- **Molecules have the tendency to take the orientation that maximises the attractive forces (+/-) and minimizes the repulsive forces (+/+) et (-/-).**

Keesom forces are also called ORIENTATION forces.

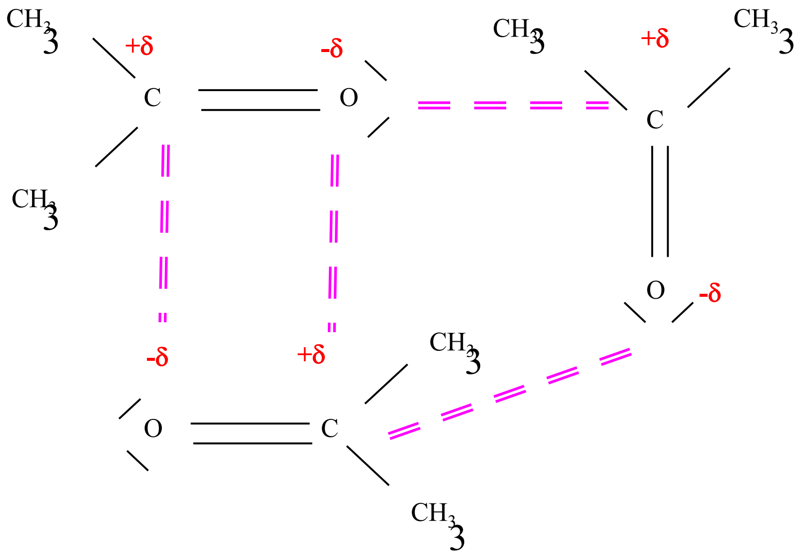


Chapter 9 – 3. Inter and intra-molecular interactions

<u>Example</u> : butane CH_3-CH_2-CH_2-CH_3 and acetone CH_3-CO-CH_3 have the same mass and very different melting and boiling temperature.

acetone ≡ polar molecule
butane ≡ non polar molecule

butane $T_{melting}$ = - 138°C ; $T_{boiling}$ = -0,5 °C (at 1 atm)
acetone $T_{melting}$ = - 95°C ; $T_{boiling}$ = +56 °C (at 1 atm)



- Acetone has higher melting and boiling temperature because of strong intermolecular interactions which are absent for a non polar molecule like butane.

Chapter 9 – 3. Inter and intra-molecular interactions

b/ Dispersion forces (LONDON forces)

- It has been shown experimentally that rare gazes or H_2 become liquid and even solid at low temperature.
- Keesom forces cannot be invoqued since neutral atoms as Ar, Ne and symetric molecules like H_2 are non polar.
- Dispersion forces are responsible for the extra cohesion that enables those species to became liquid and solid.

LONDON forces

To exist as a liquid, H_2 must be cooled below hydrogen's critical point of 33 K. (90 K for O_2, 77 K for N_2, 4 K for He)

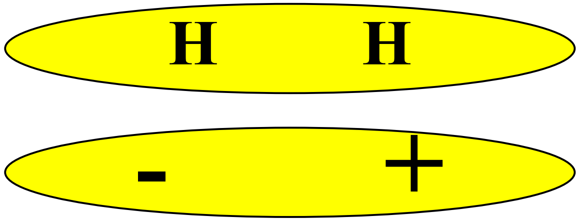
Ariane 5 emporte dans son immense réservoir central 162 tonnes d'oxygène liquide à -183°C et 28 tonnes d'hydrogène liquide à -252,87°C

Chapter 9 – 3. Inter and intra-molecular interactions

Dipolar moments different from zero appear momentaneously even for non polar molecules. Those temporary dipoles are responsible for LONDON forces

Ex : non polar H_2

At time t : Instataneous dipole
or induced dipole



A general phenomenon:

- London forces are the only interactions between non polar molecules.
- In the case of polar molecules, London forces occur in addition to Keesom forces.

3-2) Hydrogen Bonds (hydrogen interactions)

- **hydrogen interactions** occur when a hydrogen atom is connected to a small very electronegative atom X like F, O or N (and sometimes Cl or S).

- X – H bonds are strongly polarized: $X^{\delta -} – H^{\delta+}$

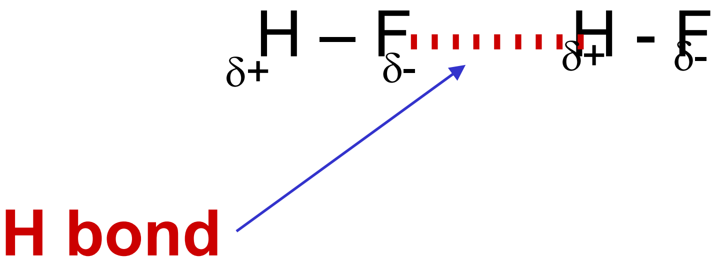
- Dipolar interactions are efficient for small atoms.

- The interaction energy can be as high as 10-40 $kJ.mol^{-1}$, close to covalent bond energies (100 - 400 $kJ.mol^{-1}$) and therefore are called:

Hydrogen Bonds

Chapter 9 – 3. Inter and intra-molecular interactions

Example:



$_{\delta+}H – F_{\delta-} \cdots\cdots H_{\delta+} - F_{\delta-}$

H bond

- The interaction occurs between **atome $H^{\delta+}$ and the lone pairs of atome $F^{\delta-}$**
- **Hydrogen Bonds can be:**

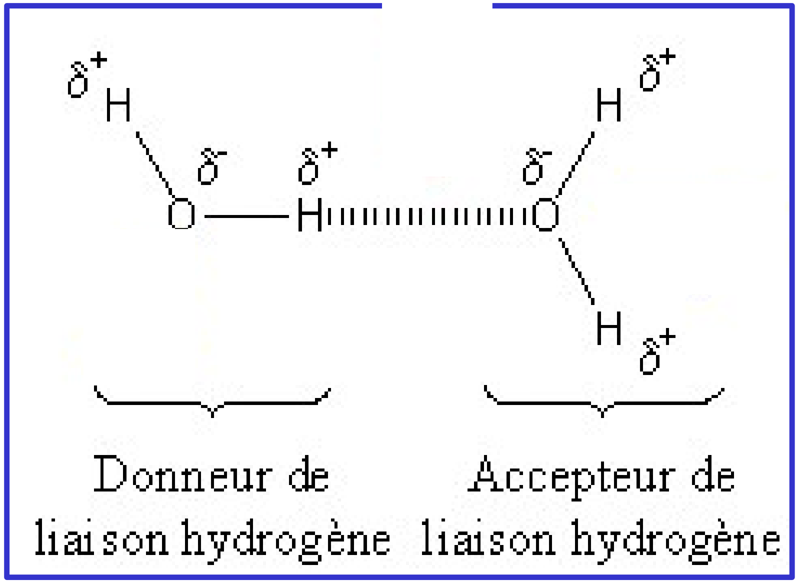
  INTER- molecular

  INTRA- molecular

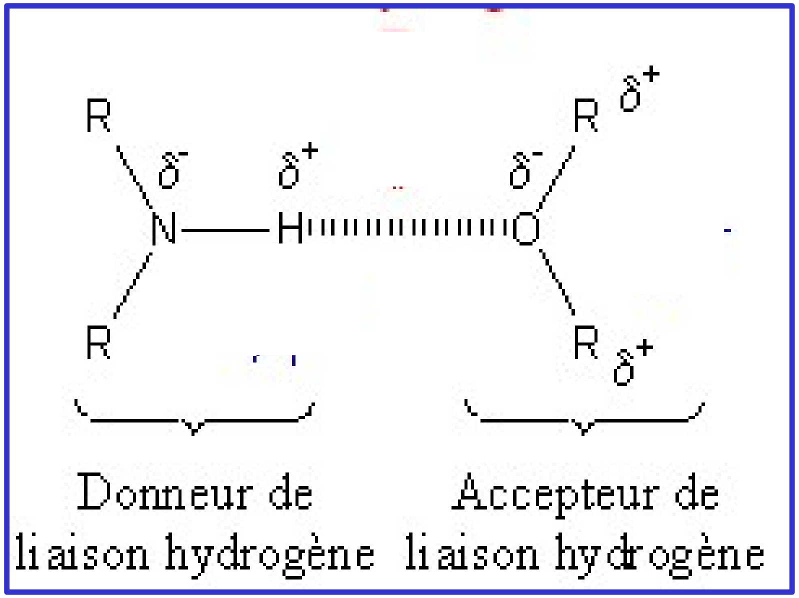
Hydrogen Bonds: INTER - molecular

Establish between :

*** identical molecules**

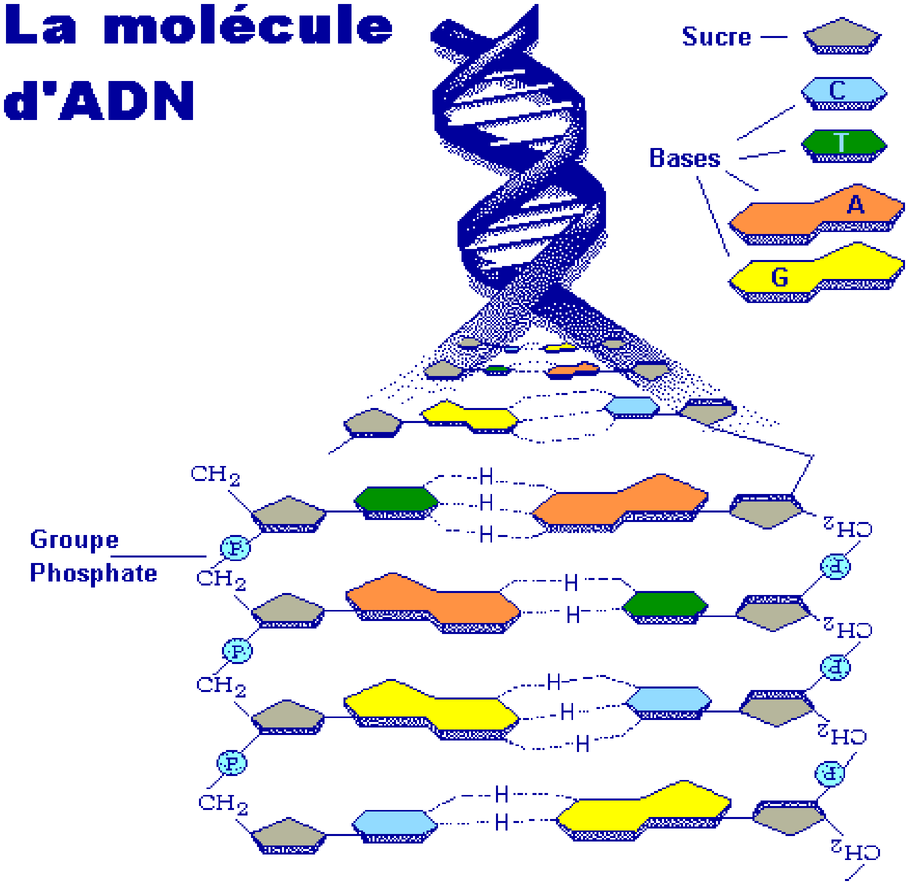


*** different molecules**



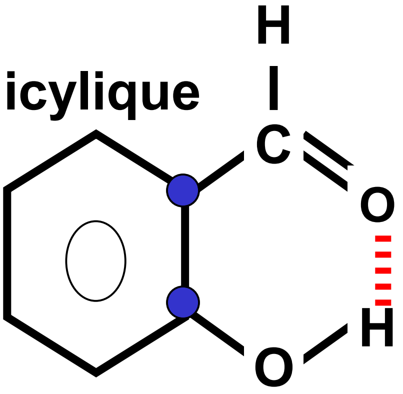
Hydrogen Bonds

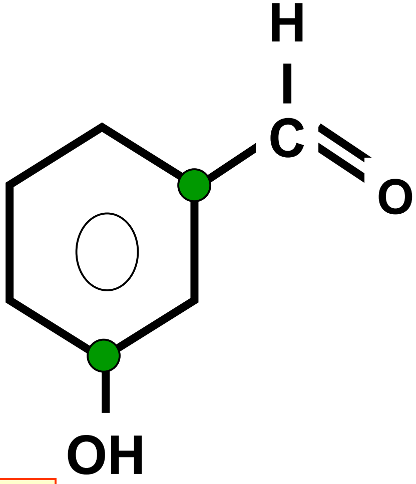
- Occur in protein chains which can interact at different positions.
    - Are responsable for the double helix structure of DNA.

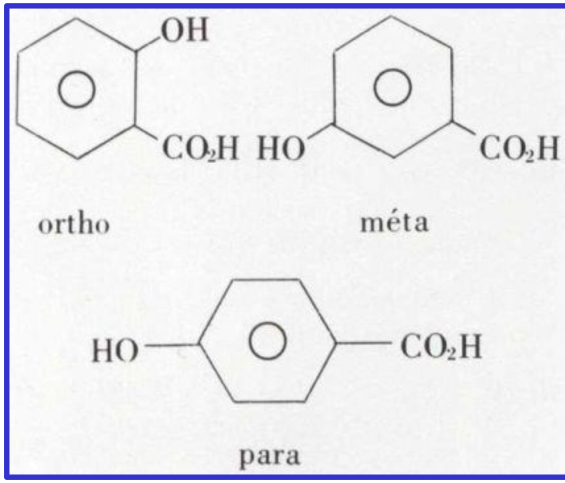


Hydrogen Bonds INTRA- molecular

Example :
Aldéhyde salicylique







Substituants are in the ortho position in the cycle

Intramolecular hydrogen bonds are possible. Inter molecular interactions are less effective.

T_m = - 7°C

Substituants are in a méta position in the cycle

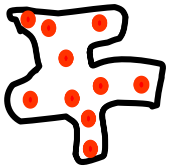
Intramolecular hydrogen bonds are NOT possible. Inter molecular interactions are more effective.

T_m = 106 °C

Physical properties are modified by weak interactions

Chapter 9 – 4. Consequences of interactions

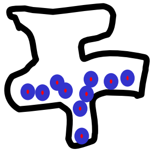
4-1) Cohesion of matter



Gaseous state

No fixed volume,
No proper shape

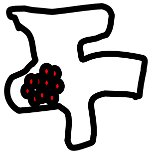
No interactions
between molecules



Liquid state

Fixed Volume
No proper shape

Weak interactions
between molecules



Solid state

Fixed Volume
Proper shape

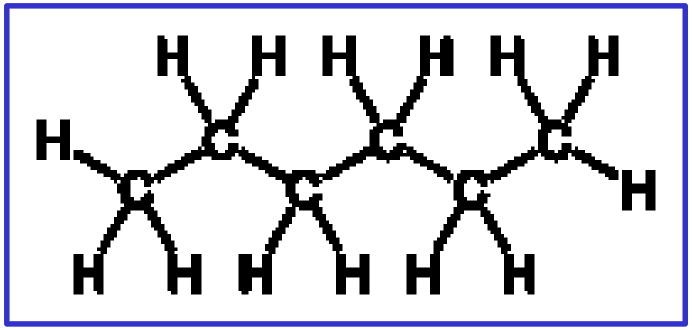
Strong interactions
between molecules

Only INTER-molecular interactions can explain the cohesion of liquid and solid molecular states.

Chapter 9 – 4. Consequences of interactions

Example 1: Hexane = non polar molecule

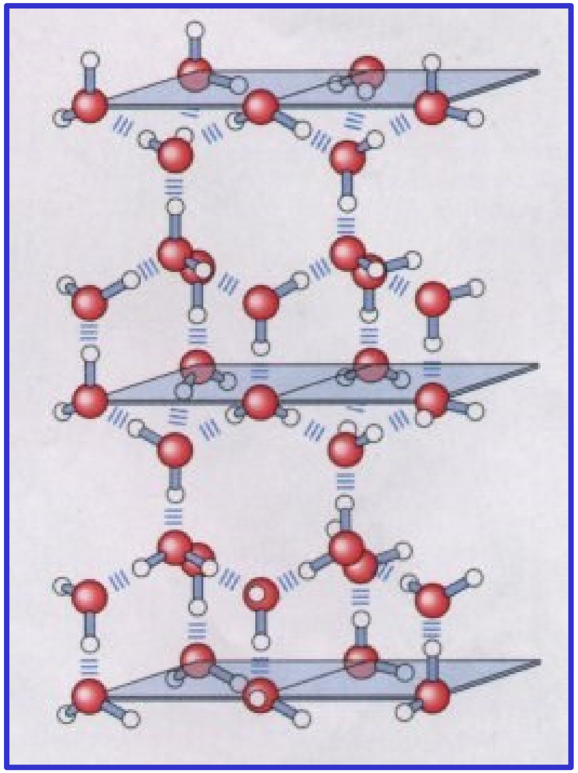
It’s a liquid because of dispersion forces.

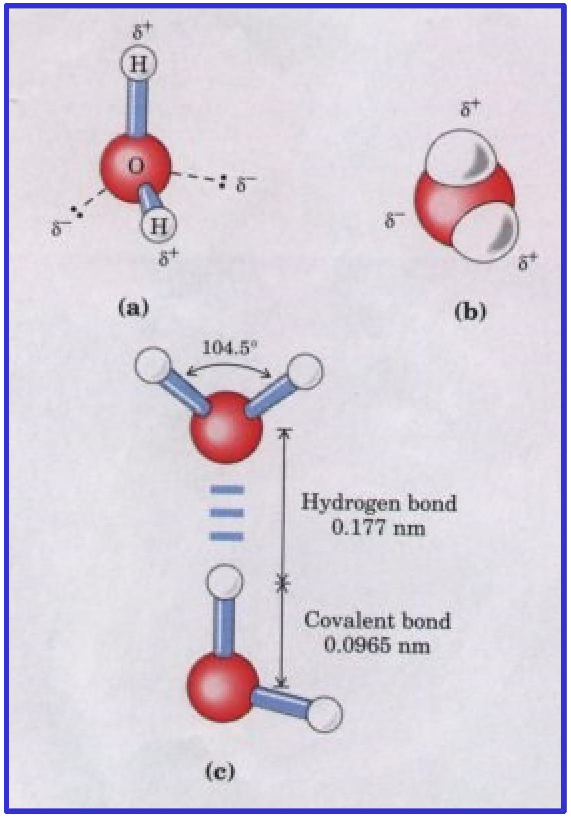


Exemple 2: Water ice = molecular solid

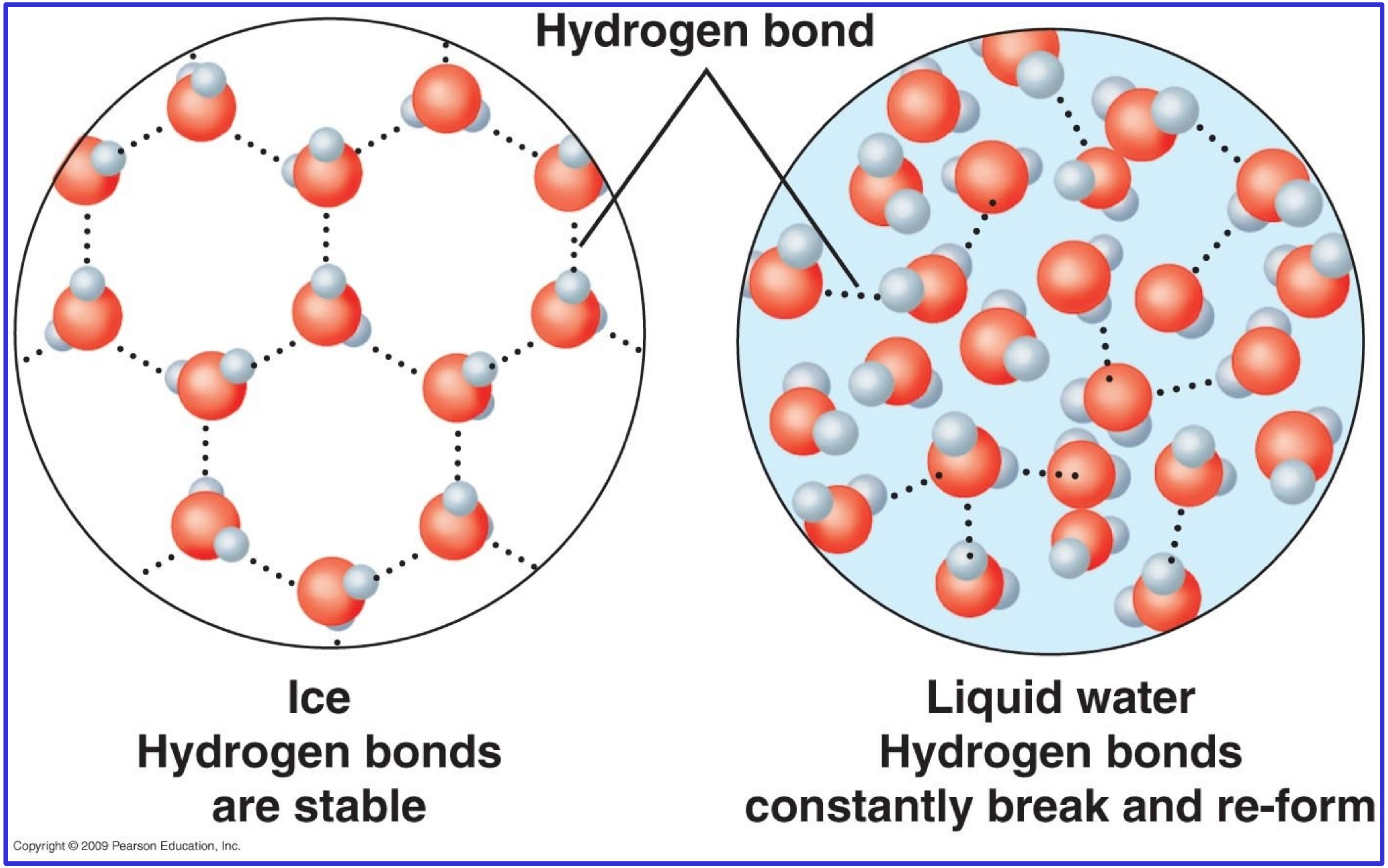
Cohesion due to H bonds

Each Oxygen atom is the central atom surronded by 4 hydrogen atoms in a tetrahedral geometry.

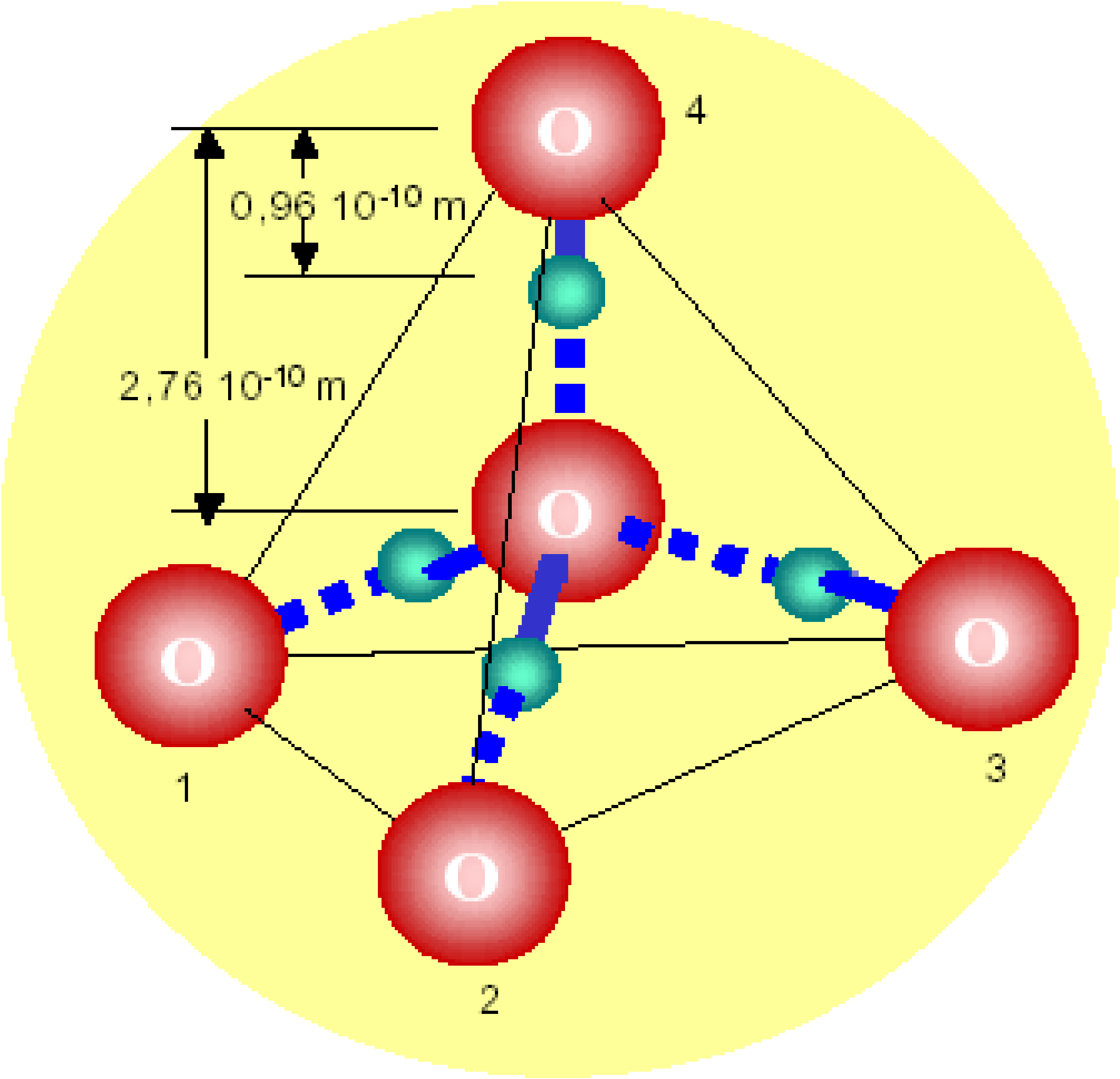




Cohesion of water ice compared to liquid water.



Water ice Structure



4-2) Melting and boiling temperature of molecular compounds

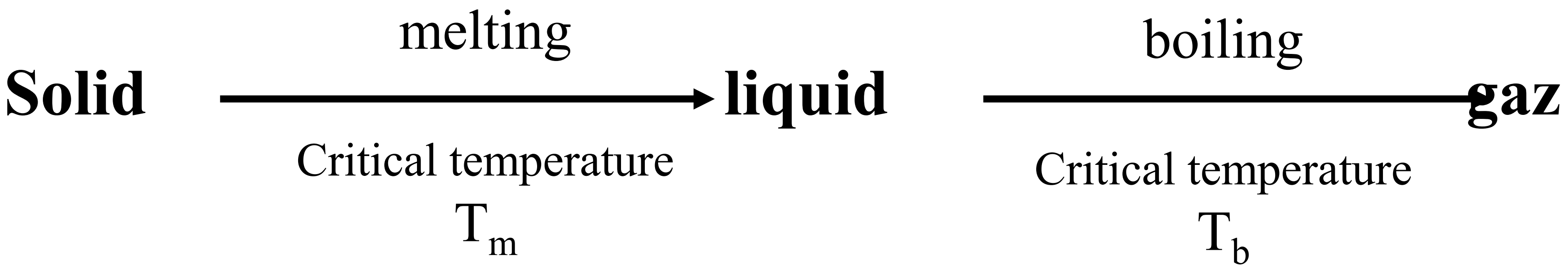
$$\textbf{Solid} \xrightarrow[\substack{\text{Critical temperature} \\ \text{Tm}}]{\text{melting}} \textbf{liquid} \xrightarrow[\substack{\text{Critical temperature} \\ \text{Tb}}]{\text{boiling}} \textbf{gaz}$$

Low energy interactions have consequences on state transition temperatures of molecular compounds

« RULE » n° 1 :

For a given serie of compounds with similar chemical properties (alcanes, alcohols,…), the melting or boiling temperature increases with the mass (consequence of London dispersion forces which exist for all compounds.)

Chapter 9 – 4. Consequences of interactions



Solid $\xrightarrow{\text{melting}}$ **liquid** $\xrightarrow{\text{boiling}}$ **gaz**

Critical temperature T_m

Critical temperature T_b

Example

- Halogens
  - Cl_2: $M = 71$ g.mol^{-1} ($T_m = -101.5°C$, $T_b = -35°C$): Gas at RT and atmospheric pressure
  - Br_2: $M = 160$ g.mol^{-1} ($T_m = -7.2°C$, $T_b = 59°C$): Liquid at RT and atmospheric pressure
  - I_2: $M = 254$ g.mol^{-1} ($T_m = 113.7°C$, $T_b = 184.3°C$): Solid at RT and atmospheric pressure
- Alcanes
  - CH_4 $M = 16$ g.mol^{-1} ($T_b = -161°C$): Gas at RT and atmospheric pressure
  - C_2H_6 $M = 30$ g.mol^{-1} ($T_b = -88°C$): Gas at RT and atmospheric pressure
  - C_3H_8 $M = 44$ g.mol^{-1} ($T_b = -42°C$): Gas at RT and atmospheric pressure

Chapter 9 – 4. Consequences of interactions

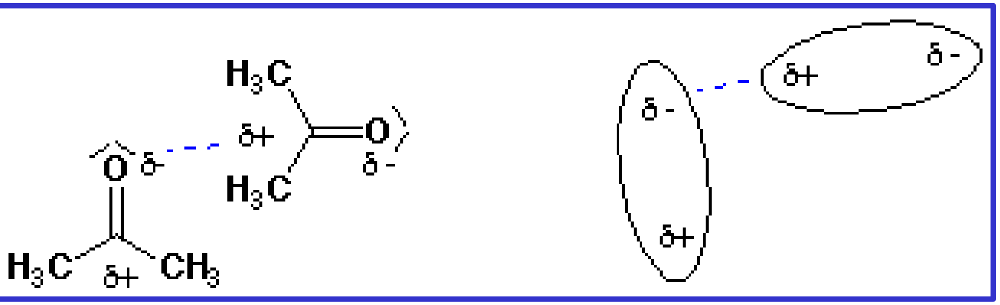
« RULE » n°2 :

The presence of dipole-dipole interactions (Keesom forces) or intermolecular hydrogen bonds increases the melting and boiling temperatures (extra energy is necessary to separate the interacting molecules)

Examples :

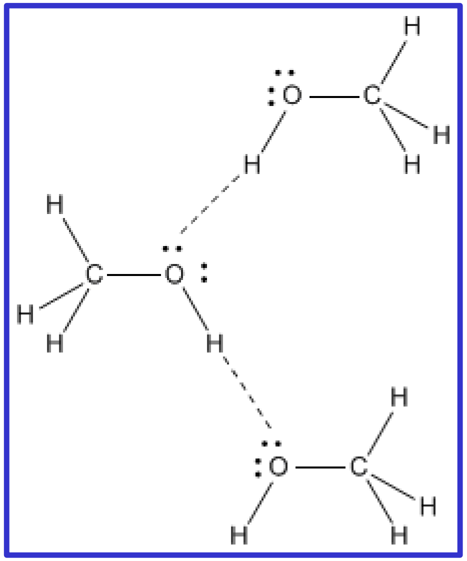
Butane : C_4H_{10} (58 g.mol^{-1}) Tb = - 0,5 °C

Propanone $(CH_3)_2$ C=0 (58 g.mol^{-1}) Tb = + 56 °C



Ethane: H_3C — CH_3 (30 g.mol^{-1}) Tb = - 89 °C

Méthanol: H_3C — OH (32 g.mol^{-1}) Tb = + 64 °C

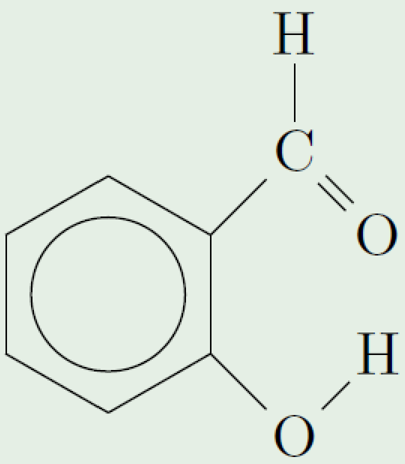


Chapter 9 – 4. Consequences of interactions

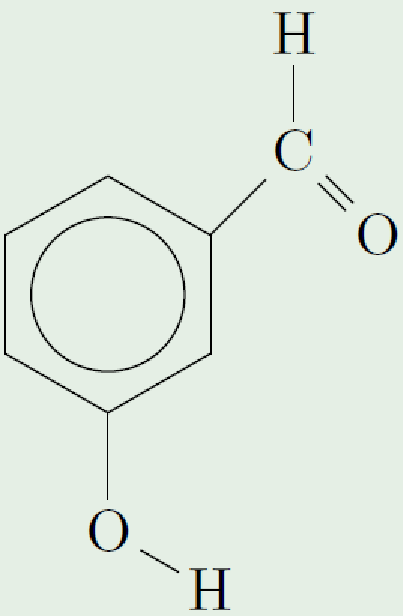
« RULE » n°3 :

Presence of intra-molecular interactions diminishes the melting and boiling temperatures.

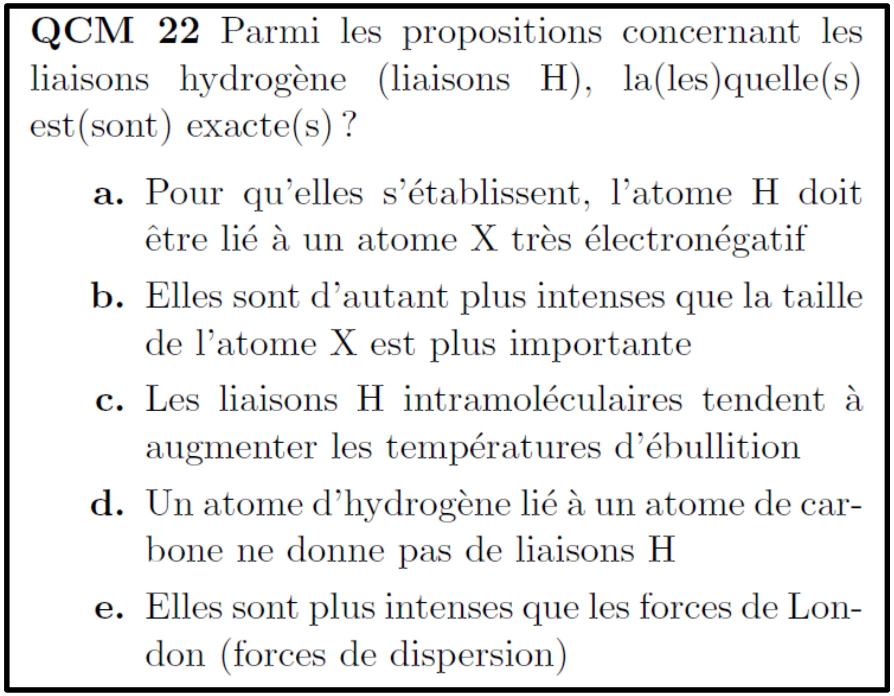
Example



intramolecular hydrogen bond: few intermolecular hyd. bond ortho: $T_m = -7°C$



no intramolecular hydrogen bond: lot of intermolecular hyd. bond méta: $T_m = +106°C$



QCM 22 Parmi les propositions concernant les liaisons hydrogène (liaisons H), la(les)quelle(s) est(sont) exacte(s) ?

- **a.** Pour qu'elles s'établissent, l'atome H doit être lié à un atome X très électronégatif
- **b.** Elles sont d'autant plus intenses que la taille de l'atome X est plus importante
- **c.** Les liaisons H intramoléculaires tendent à augmenter les températures d'ébullition
- **d.** Un atome d'hydrogène lié à un atome de carbone ne donne pas de liaisons H
- **e.** Elles sont plus intenses que les forces de London (forces de dispersion)

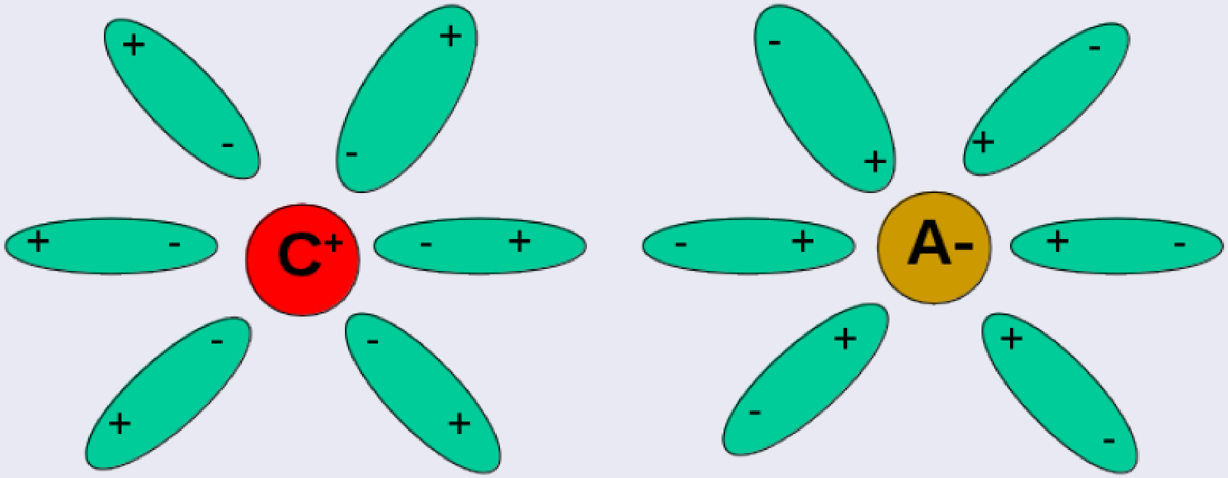
IV-3) Ions solvatation

Ions solvatation

Water is a permanent dipole

In water, an ion gets surrounded by water molecules thanks to ion/dipole interaction

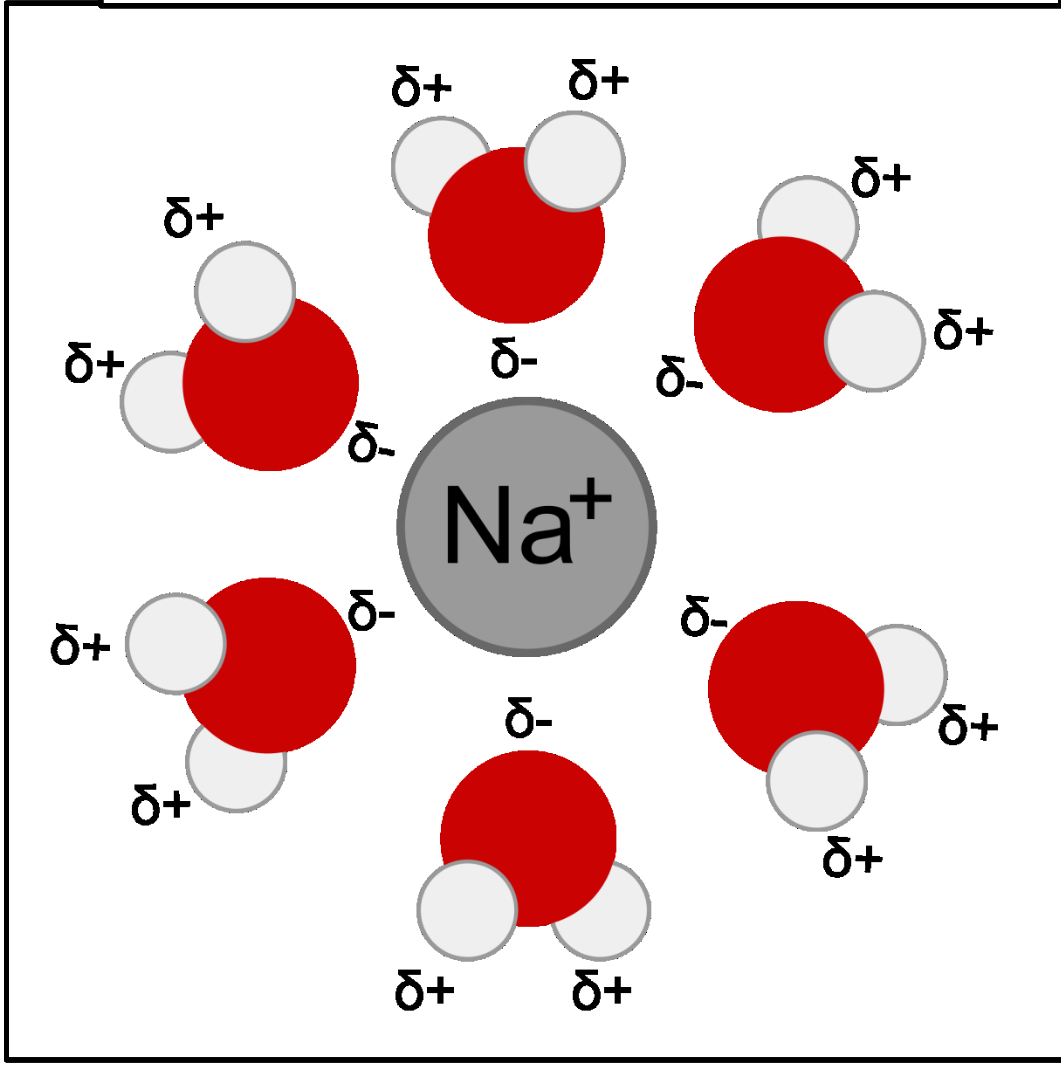
This prevents ions of opposite sign to recombine: this is the hydratation phenomenon



Chapter 9 – I. Consequences of Interact

Is sucrose soluble or insoluble in water?

It also takes **energy** to break the **hydrogen bonds** in **water** that must be disrupted to insert one of these **sucrose** molecules into solution. Sugar dissolves in **water** because energy is given off when the slightly polar **sucrose** molecules form **intermolecular bonds** with the polar **water** molecules.



A sodium ion solvated by water molecules.

QCM 20 On considère deux alcool, le méthanol CH_3-OH noté 1 et propanol $CH_3CH_2CH_2-OH$ noté 2 dont les températures d'ébullition sont respectivement $T_{eb_1} = 65°C$ et $T_{eb_2} = 97°C$. Sachant que $Z_{\mathrm{H}} = 1$, $Z_{\mathrm{C}} = 6$, $Z_{\mathrm{O}} = 8$, $E_H^- = 2,1$, $E_C^- = 2,5$ et $E_O^- = 3,5$, quelle(s) est (sont) la (les) proposition(s) exacte(s) :

- **a.** Ce sont essentiellement les forces de London qui expliquent que T_{eb_2} est plus élevée que T_{eb_1}
- **b.** Pour chacun de ces composés, il peut s'établir des liaisons hydrogène intramoléculaires
- **c.** Pour chacun de ces composés, il peut s'établir des liaisons hydrogène intermoléculaires
- **d.** Le méthanol et le propanol sont des composés polaires
- **e.** Si la pression est égale à 1 bar, le méthanol et le propanol sont gazeux à la température ambiante.