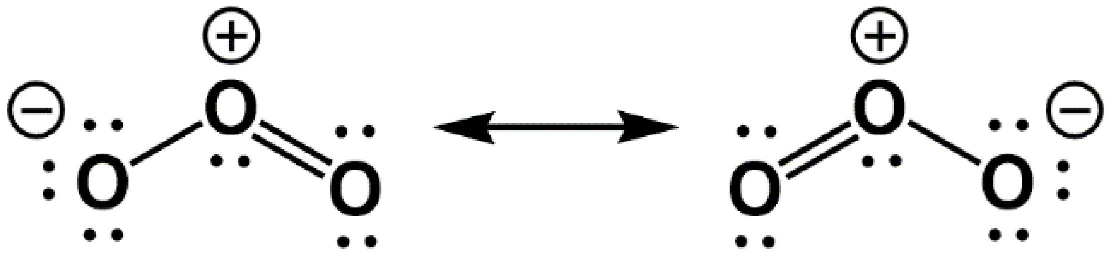
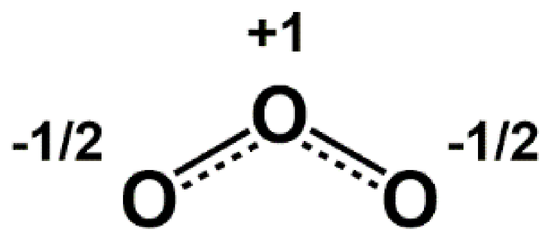
Resonance structures

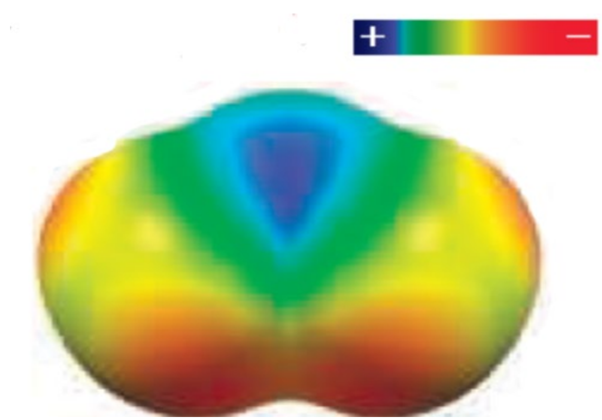
- **Lewis structures**



- **Resonance hybrid**



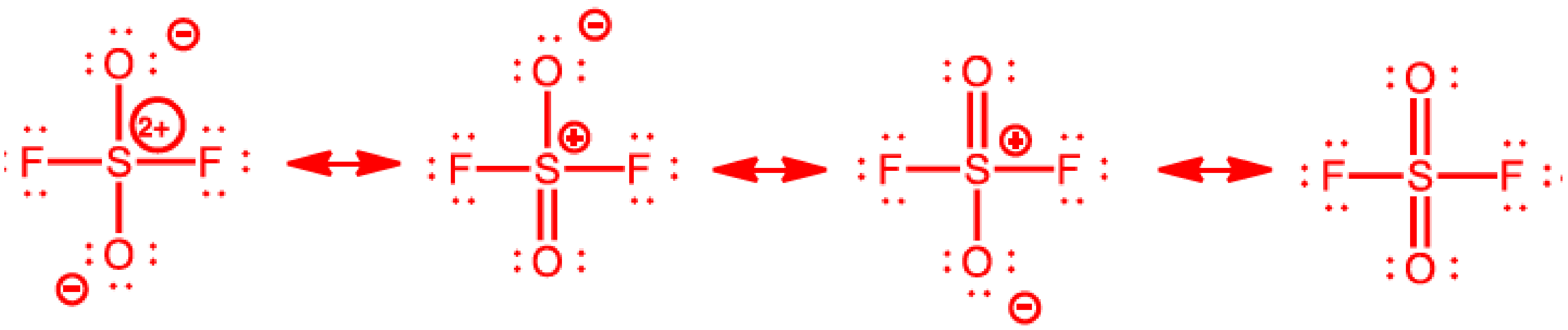
- **Real Electron Density**



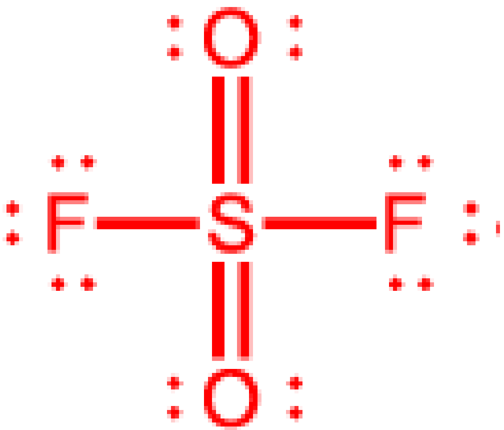
Chemistry by Zumdahl, Zumdahl, DeCoste

Draw **ALL** chemically reasonable Lewis structures of SO_2F_2

- Draw all structures that follow the octet rules and place negative charges on the most electronegative atom and the positive charges on the least electronegative atom.
- Those without the formal charges minimized are still chemically reasonable but they do not contribute significantly to the resonance hybrid.



Draw the **most stable** Lewis structures of SO_2F_2



Unit 4
Intermolecular Interactions

Slide Color Codes

All Lectures

Section Only

Required

Required

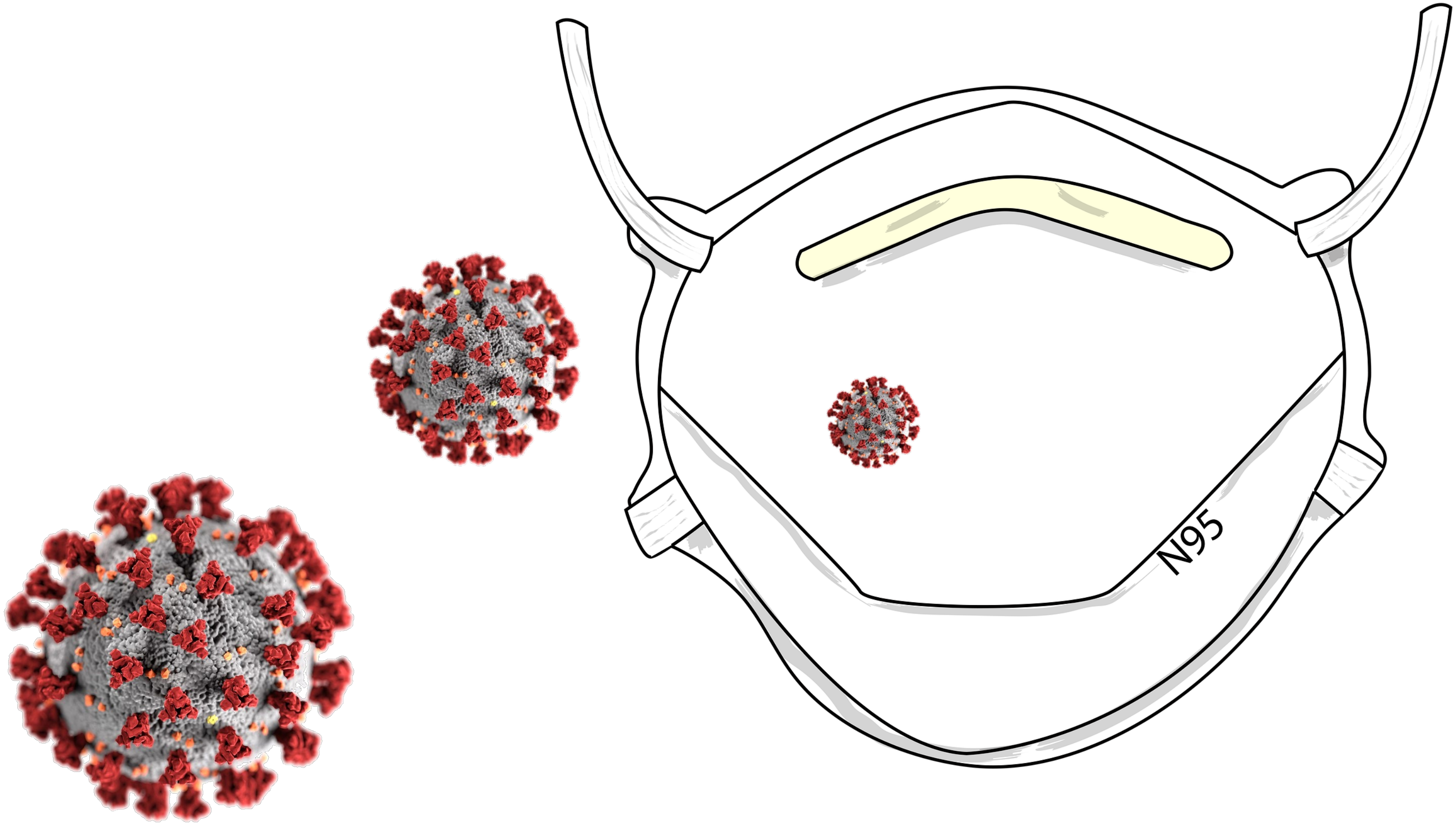
OK to Skip

Useful

Not Examable

Blueprint question

How does an N95 mask stop a virus in it's tracks?



Learning Objectives

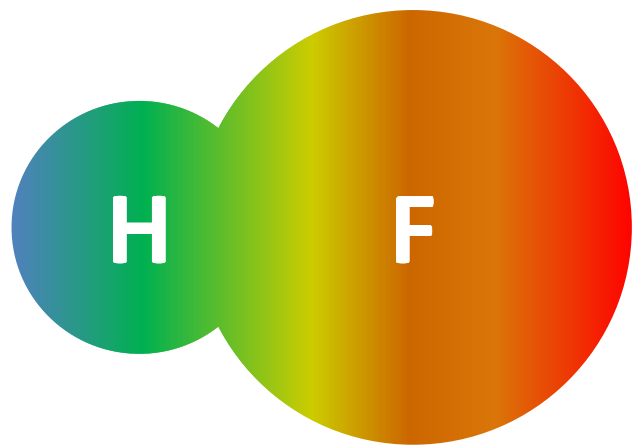
- Predict the polarity of a molecule from its molecular geometry and bond polarity.
- Predict the types of intermolecular forces likely to be most important for a particular substance.

Bond Polarity

Because of differences in electronegativity, electrons are never equally distributed when two different atoms bond. This charge separation is known as a dipole. Bonds with a dipole are called **polar bonds**.

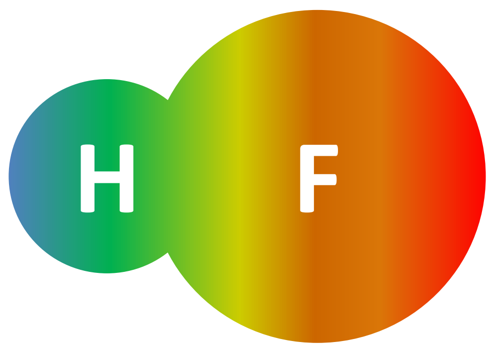
High electron density

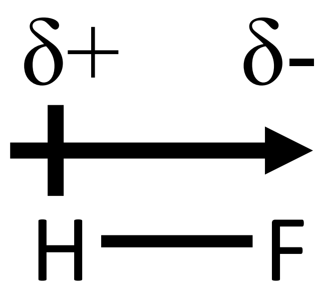
Low electron density



Representation of Bond Polarity

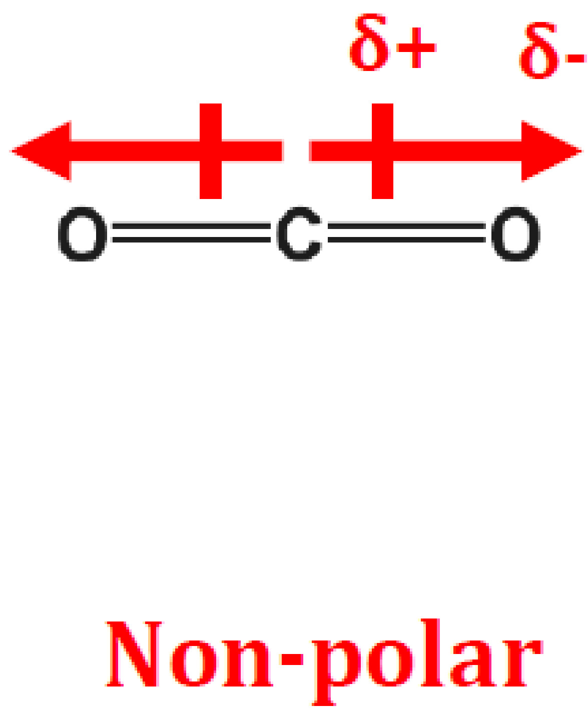
- An arrow pointing towards the most electronegative atom is used to show bond polarity. The end of the arrow with the most electron density has the label δ- while the other end has the label δ+





Molecular polarity

- The polarity of a molecule depends on the three dimensional arrangement of atoms. For example, although the C=O bond is polar, the CO_2 molecule is non-polar.

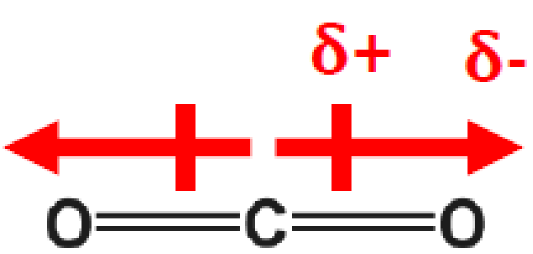


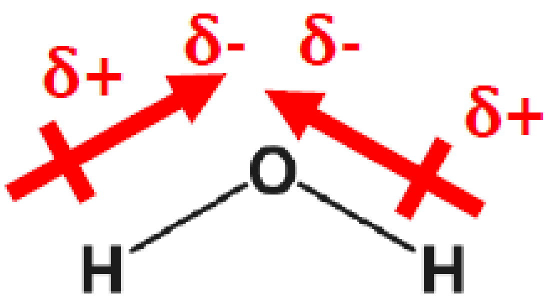
Determining molecular polarity

1. Draw the VSEPR <u>molecular shape</u> of the molecule
2. Draw arrows to show <u>bond dipoles</u> for each bond in a molecule
3. Do a <u>vector addition</u> for each dipole drawn
4. If the vector addition is zero, the molecule is non-polar. If the vector addition is non-zero, the molecule is polar

Worksheet Question #1

Add arrows to show bond dipoles for the following polar covalently bonded compounds. Add δ+ and δ- to the following structures. Lone pairs are NOT shown. Determine which molecules are polar and which are non-polar.



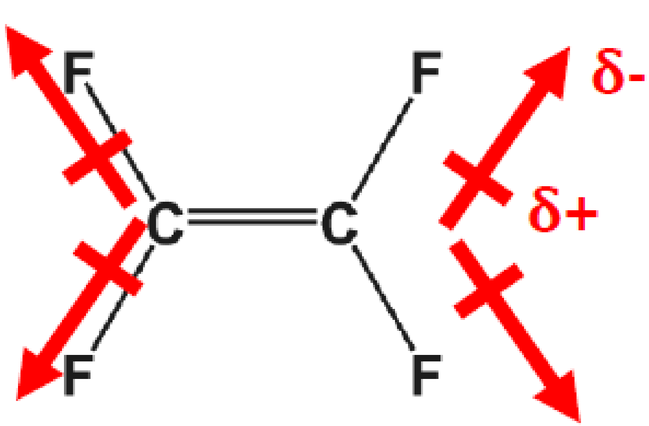


Non-polar

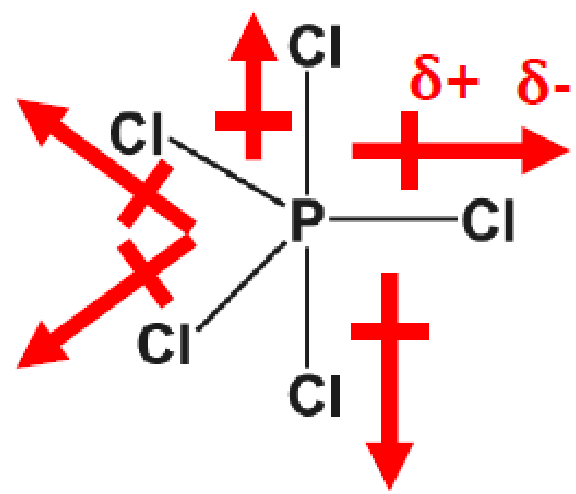
Polar

Worksheet Question #1

Add arrows to show bond dipoles for the following polar covalently bonded compounds. Add δ+ and δ- to the following structures. Lone pairs are NOT shown. Determine which molecules are polar and which are non-polar.



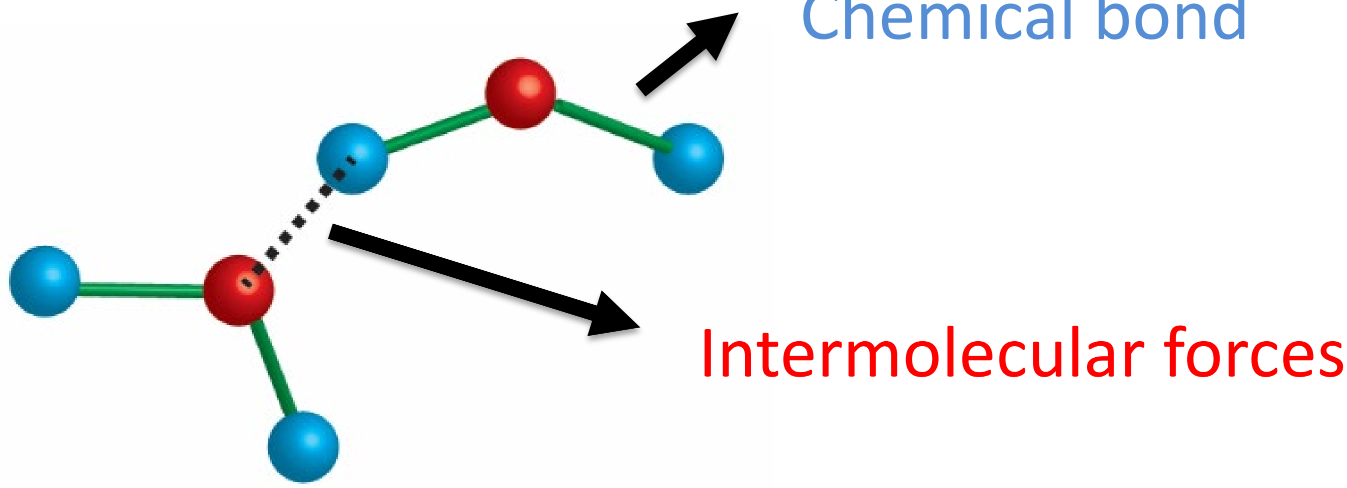
Non-polar



Non-polar

Chemical Bonds vs. Intermolecular Forces

- **Chemical Bonds:**
  - ❑ Ionic bonds (300-700 kJ mol^{-1})
  - ❑ Covalent bonds (100-500 kJ mol^{-1})
- **Intermolecular Forces**



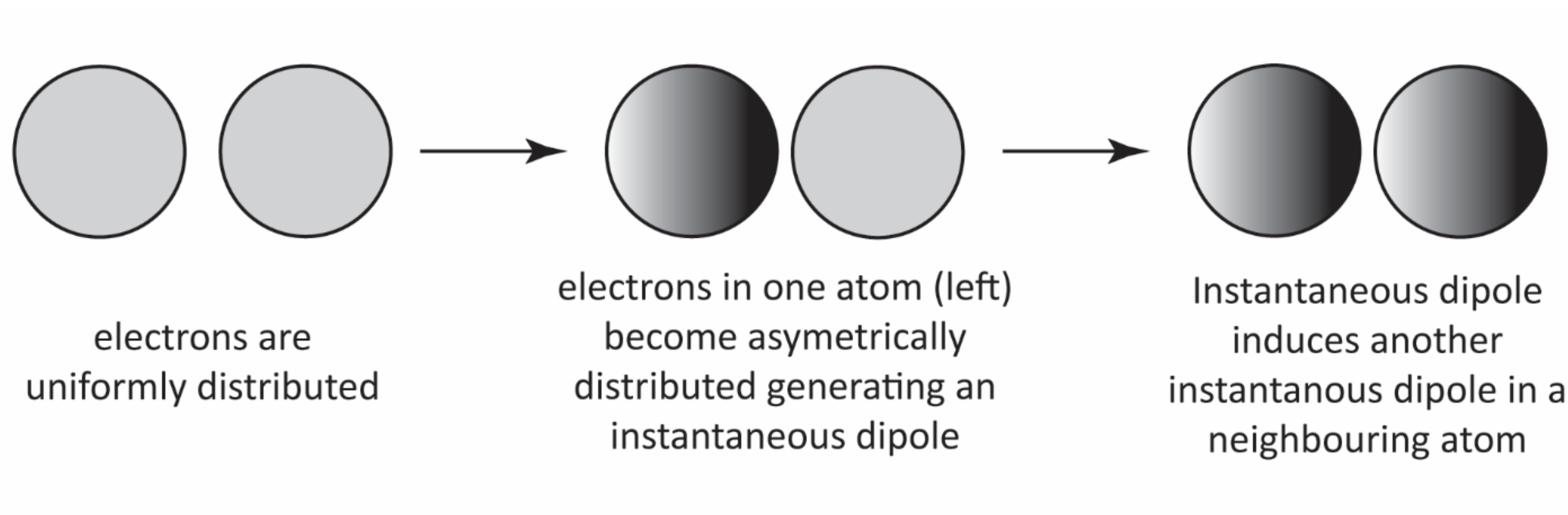
  - Energy required to vaporize H_2O: 41 kJ mol^{-1}
  - Bond energy of O-H bond in H_2O: 463 kJ mol^{-1}

Intermolecular Forces

- London dispersion forces
- Dipole-dipole forces
- Hydrogen bonding
- Charge-dipole (or ion-dipole) forces
- Charge-charge (or ion-ion) forces

London Dispersion Forces

- Also known as <u>instantaneous dipole-induced dipole forces</u>, they exist between all atoms and molecules, and are always attractive. Arise from a momentary asymmetry in electron density caused by charge fluctuations.



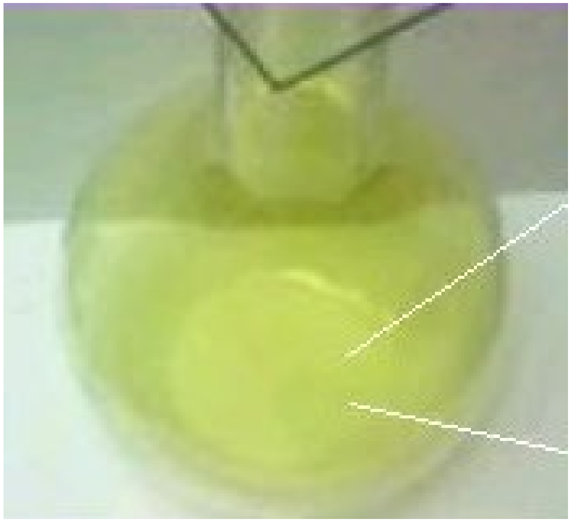
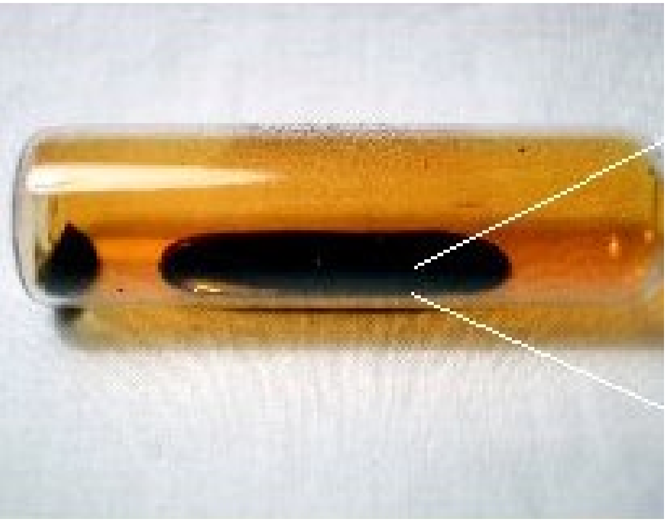
Electric Polarizability

- Measures how large a dipole can be induced by an external electric field. Polarizability is greater in species with more weakly bound or delocalized electrons, thus favouring dispersion.

Halogen Species	Melting Point
F_2	-219.62°C
Cl_2	-101.5°C
Br_2	-7.3°C
I_2	113.7°C

- Non-polar species only London-dispersion (LD) forces.
- The higher melting point, the greater the LD forces.
- Therefore, I_2 has highest LD and F_2 has lowest LD.

Polarizability


Cl_2 Br_2 I_2 $\longrightarrow$

London dispersion forces increase

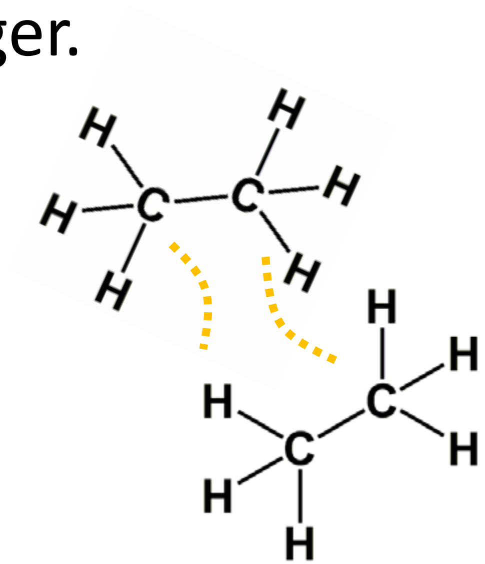
Boiling points

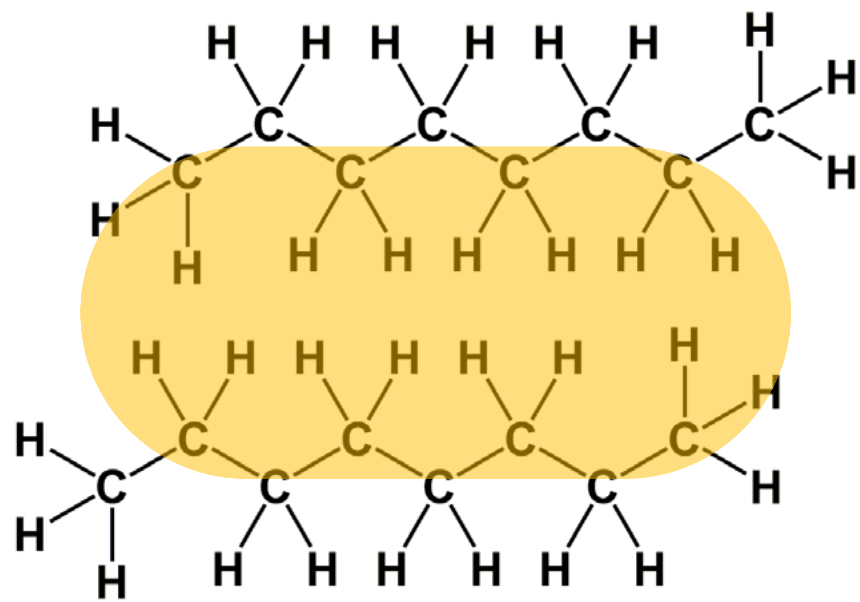
Noble Gas	Boiling Point (K)
Helium	4.2
Neon	27.1
Argon	87.3
Krypton	120.9
Xenon	166.1
Radon	211.5

- Non-polar species: only London-dispersion (LD) forces.
- The higher melting point, the greater the LD forces.

Boiling Points of Hydrocarbons

- **Larger molecules** have a greater number of polarizable atoms that contribute to making the total dispersion larger.





Ethane

Boiling point: -89 °C

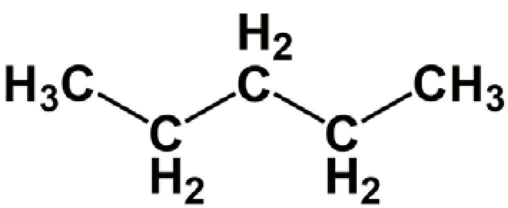
Octane

Boiling point: 125.6 °C

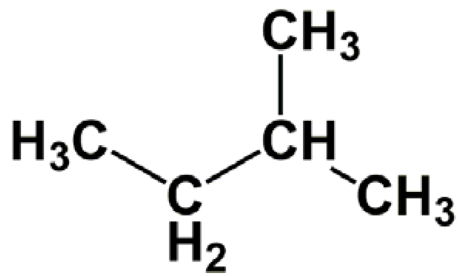
- C–H bond is ***weakly polar*** (ΔEN = 0.35), but it is often treated as **nonpolar** in practice.
- Therefore, only LD forces are considered in hydrocarbons.

Boiling Points of Hydrocarbons

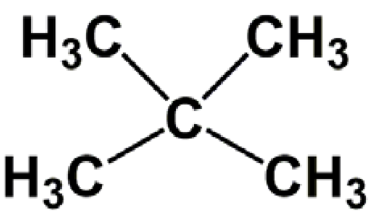
- **Branching** within a molecule reduces the possibilities for intermolecular interactions and lowers the melting/boiling points.
- Example: C_5H_{12}:



Pentane
BP: 309.2 K



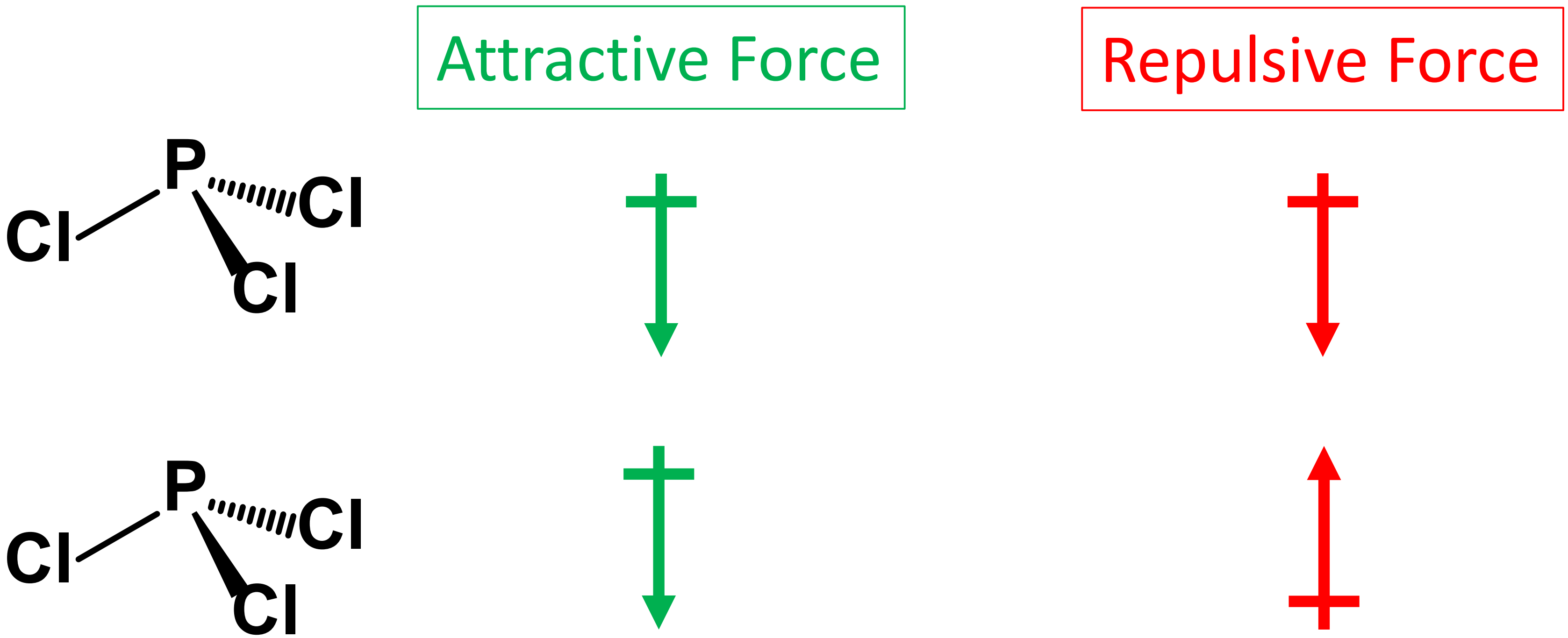
2-methylbutane
BP: 301.0 K



2,2-dimethylpropane
BP: 282.6 K

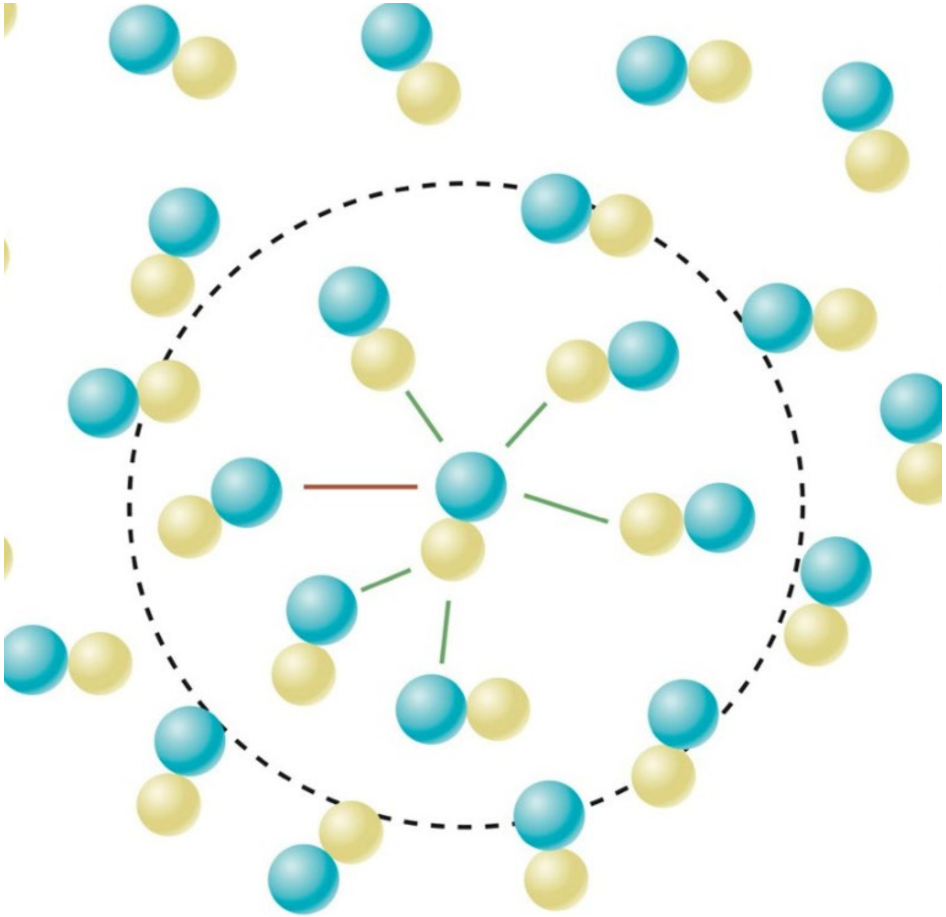
Dipole-dipole interactions

- Dipole-dipole interactions arise from favourable alignment of dipoles in molecules.
- Example:



Dipole-dipole interactions

- In a liquid there are both repulsive and attractive forces. Overall the number of attractive forces outweigh the repulsive forces



Consider NaCl

- It requires 769 kJ to separate one mole of solid **NaCl** into gaseous $Na^+$and Cl^- ions

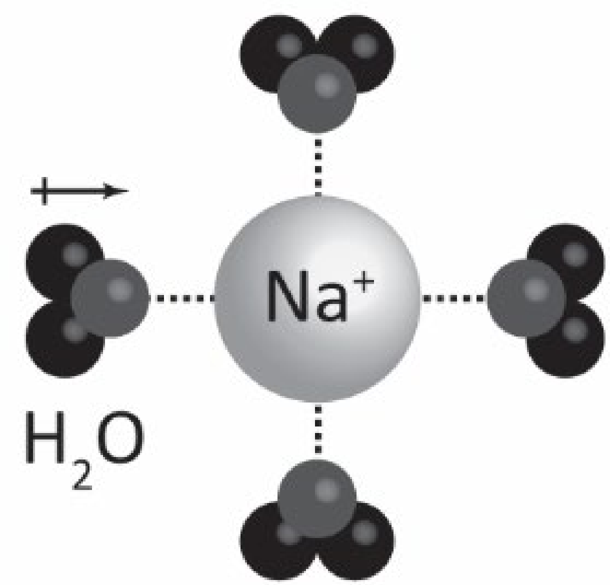
- Strongest covalent bonds known:
  C-F: 544 kJ/mol
  Si-F: 582 kJ/mol
  N=N: 418 kJ/mol
  N≡N: 942 kJ/mol

Charge-dipole interactions

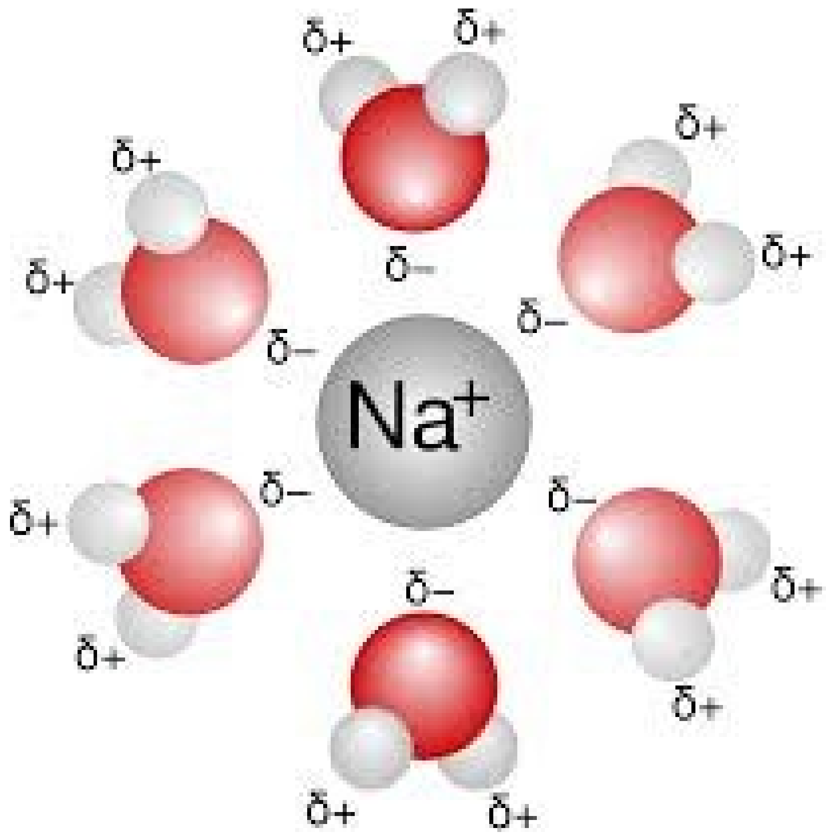
- Ions in a sea of polar molecules (e.g. H_2O)
  - a.k.a. "**solvation**" of ions
  - molecules orient to stabilize ionic charge
  - effect is about 5-20 kJ/mol *per interaction*

$$E \propto -\frac{|z|\mu}{r^2}$$

where:
z is the charge of the ion,
μ is the dipole moment, and
r is the distance between the ion and the molecule



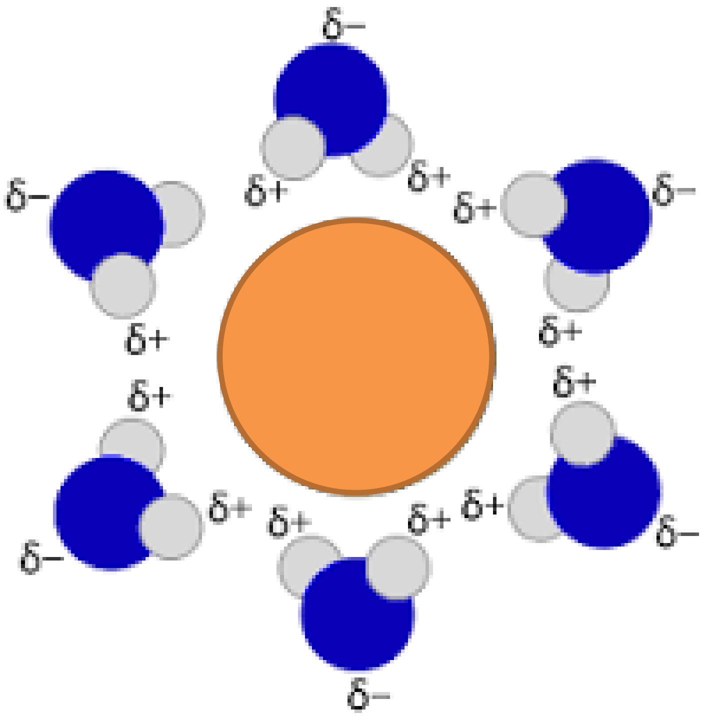
Water solvation



Clicker Question

Which dissolved ion are we looking at here - Na^+ or Cl^-?

a) Na^+
b) Cl^-



Worksheet Question #3

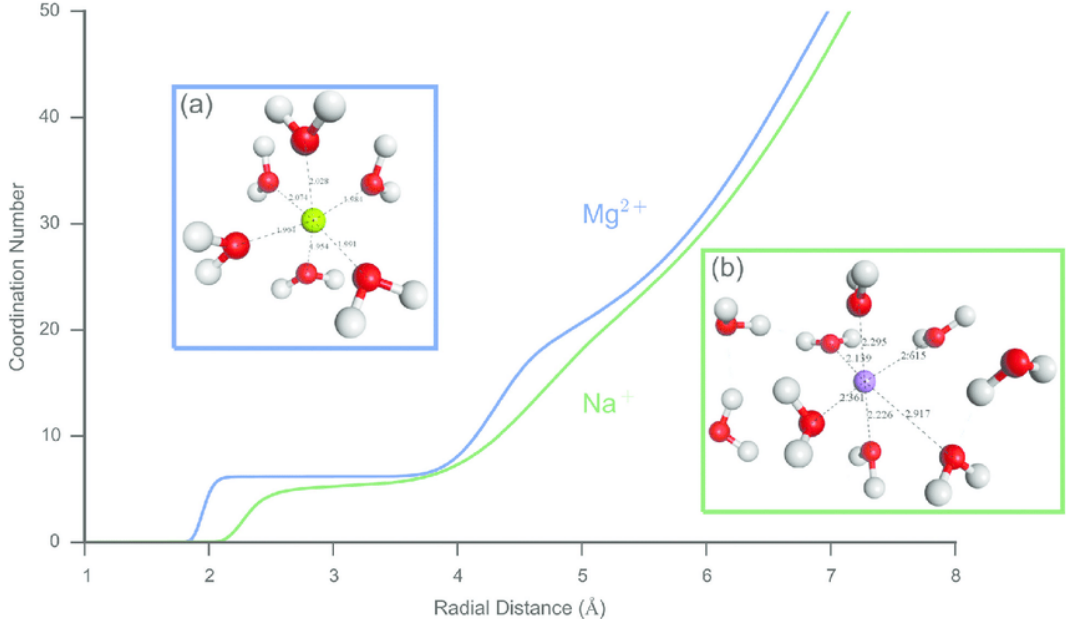
Which one experiences greater ion-dipole forces in water, Mg^{2+} or Na^{+}?

ANS: Mg^{2+}

Worksheet Question #3

Which one experiences greater ion-dipole forces in water, Mg^{2+} or Na^{+}?

Cumulative number of oxygen atoms



Mg2+ has the stronger interaction

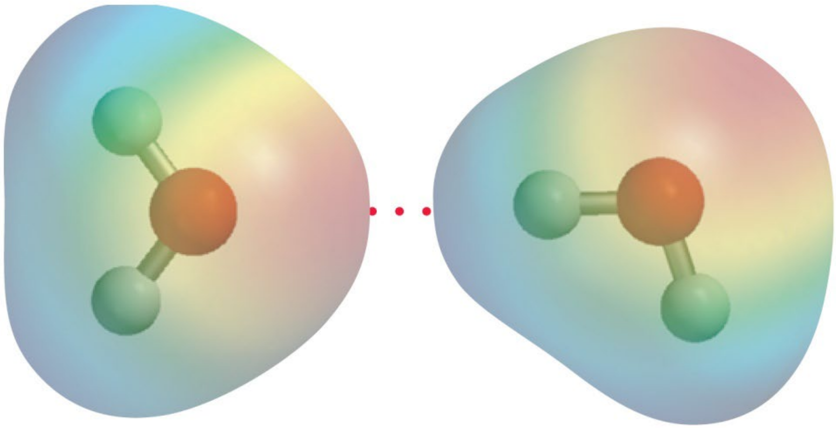
- Dynamic behaviour of the silica-water-bio electrical double layer in the presence of a divalent electrolyte, Lowe, B. M.; Maekawa, Y.; Shibuta, Y., et al., Physical chemistry chemical physics, 2017, Volume 19, Issue 4

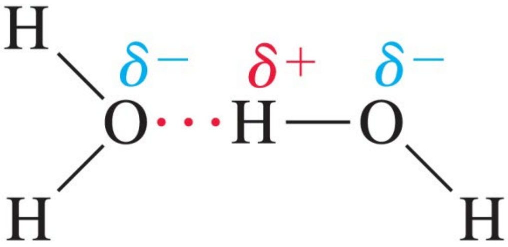
Hydrogen Bonding

A strong dipole-dipole force in molecules with a hydrogen atom bonded to an electronegative atom (**N, O, or F**).

Energy ~ 10-40 kJ/mol

H_2O





Neat application: molecular self-assembly

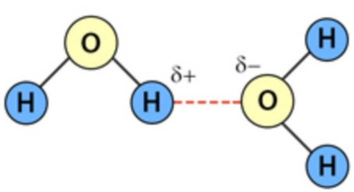
https://www.youtube.com/watch?v=G25mMDCFMwo

https://www.youtube.com/watch?v=HU_pgHlWsdc

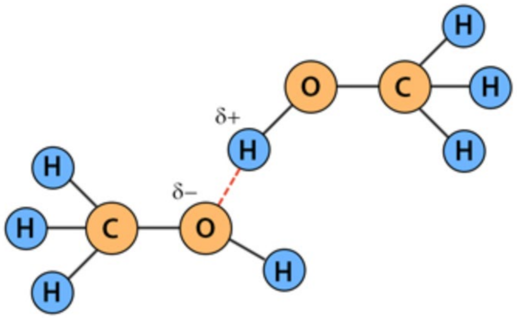
Hydrogen Bonding (HB)

Hydrogen attached to a N, O, F interacting with ANOTHER N, O, F

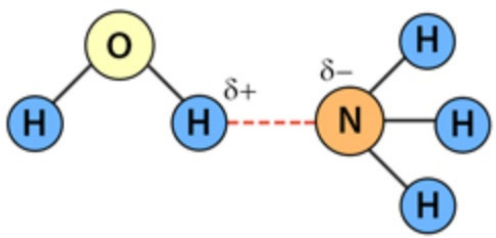
- A hydrogen atom **bonded to O, N, or F**, making the hydrogen partially positive and able to form hydrogen-bonds.
- Around 10-40 kJ/mol
- Examples:



Water



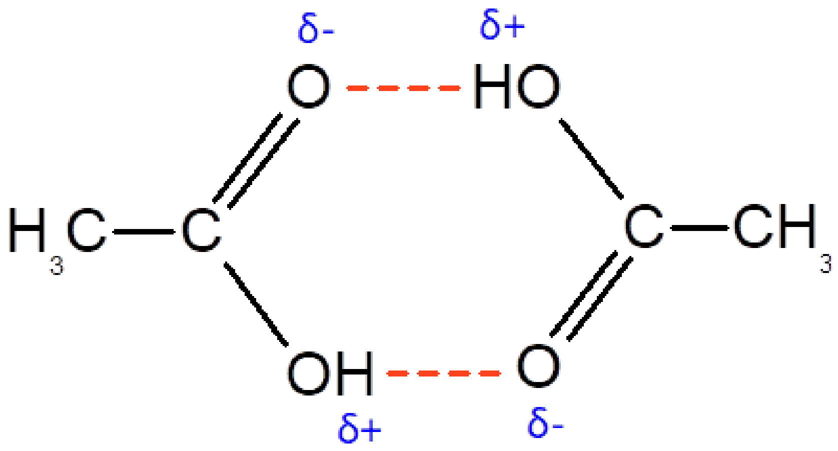
Methanol



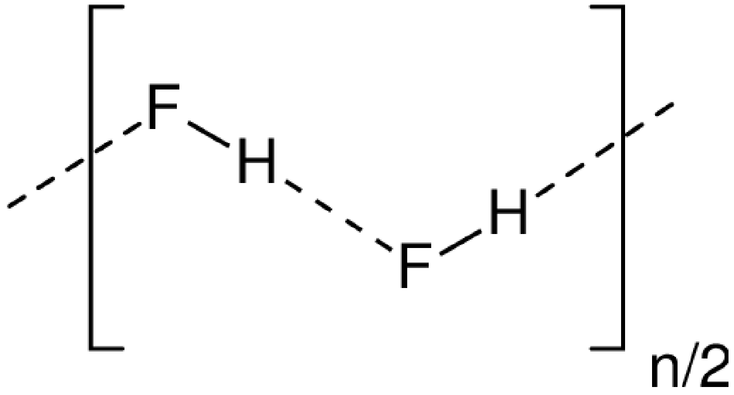
Water- ammonia

Hydrogen Bonding

- Acetic acid dimerization



- Hydrogen Fluoride chains $(HF)_n$



Clicker Question

- Which of these pure substances will **not** form hydrogen bonds?

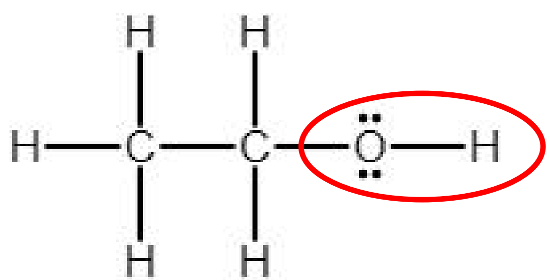
I) CH_3CH_2OH

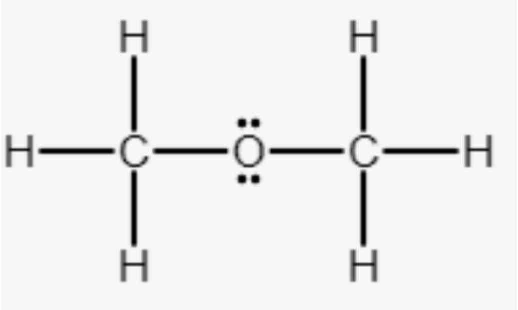
II) CH_3OCH_3

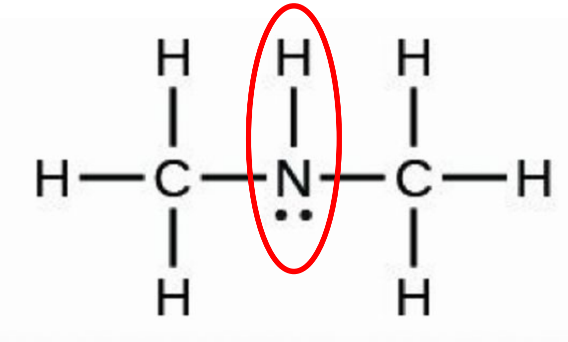
III) $H_3C-NH-CH_3$

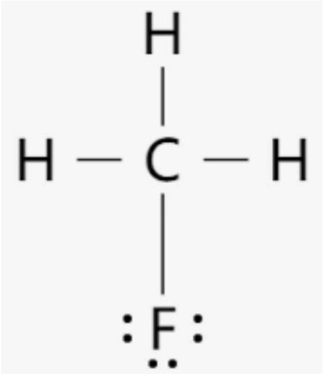
IV) CH_3F

a) I and II
b) I and III
c) II and III
d) II and IV
e) I and IV









Clicker Question

Which of the following compounds is expected to have the highest boiling point?

a) $CH_3CH_2CH_3$
b) $CH_3CH_2CH_2CH_3$
c) CH_3OCH_3
d) $CH_3CH_2NH_2$
e) CH_3CH_2F

Worksheet Question #4

Which type of intermolecular interactions need to be overcome to convert each of the following liquids to gases?

a) CH_4 London dispersion forces

b) CH_3F London dispersion and dipole-dipole interactions

c) CH_3OH London dispersion
and hydrogen bonding (also a dipole-dipole interaction)

Worksheet Question #4 - Clicker Question

Which of the molecules from WS Q2 (CH_4, CH_3F, and CH_3OH) will experience **London dispersion forces**?

A. CH_4

B. CH_3F

C. CH_3OH

D. CH_4 and CH_3F

✓ E. All of the above

(All molecules have LD forces, but it might not be the most significant interaction.)

Worksheet Question #4 - Clicker Question

Which of the molecules from WS Q2 (CH_4, CH_3F, and CH_3OH) will experience **dipole-dipole** interactions?

A. CH_4

B. CH_3F

C. CH_3OH

D. CH_3F and CH_3OH

E. All of the above

(All polar molecules have dipole-dipole interactions.)

Worksheet Question #4 - Clicker Question

Which of the molecules from WS Q2 (CH_4, CH_3F, and CH_3OH) will experience **hydrogen bonding** interactions?

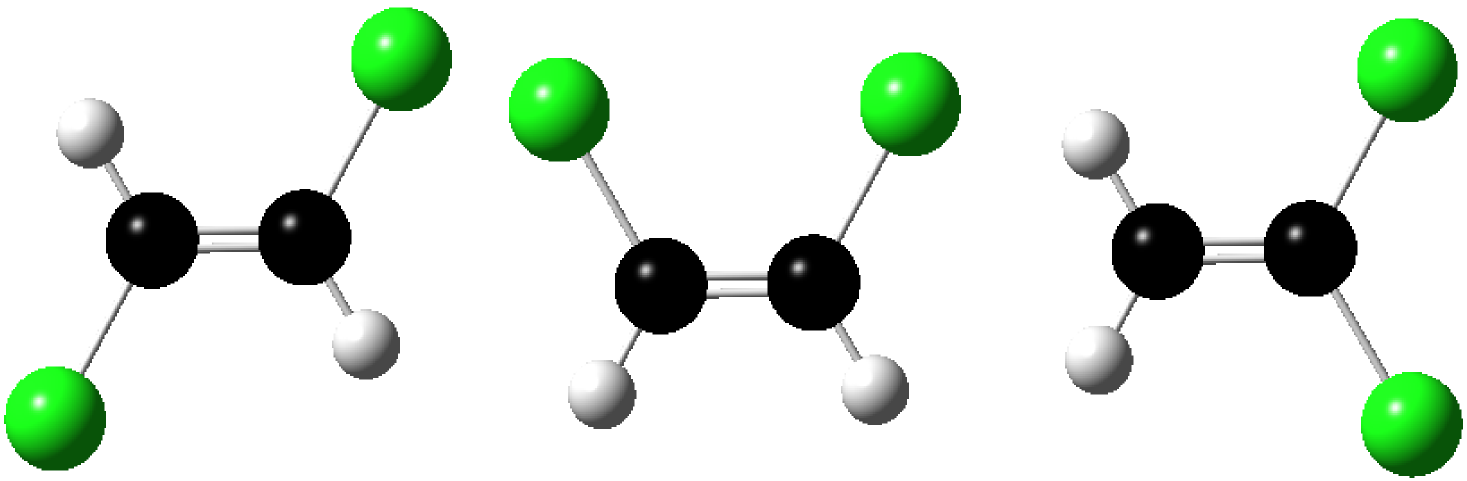
A. CH_4
B. CH_3F
C. CH_3OH
D. CH_3F and CH_3OH
E. All of the above

Summary

Force type	Strengt h	Exhibited by	Examples
London Dispersion forces	Weak	Present in all atoms and molecules. Strength increases as the number of electrons in the molecule increases (more polarizable)	$I_{2,}$ Kr, PCl_5
Dipole-dipole interactions	Strong	Molecules with a permanent dipole.	PCl_3, ICl, CH_3Cl
Hydrogen bonds	Strong	Molecules with H bonded to F, O, or N. The large electronegativity difference and resulting permanent dipole are responsible for the strength of these forces.	HF, H_2O
Charge-charge or Ion-ion interactions	Very Strong	Ionic solids or ionic liquids.	NaCl, K_3PO_4

Clicker Question

There are three isomers of $C_2H_2Cl_2$, shown as ball-and-stick models below. Which isomer experiences London Dispersion forces only?



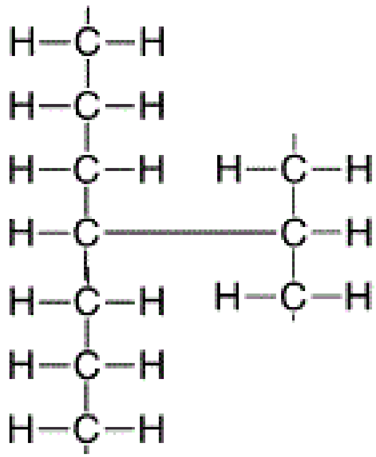
a. b. c.

✓

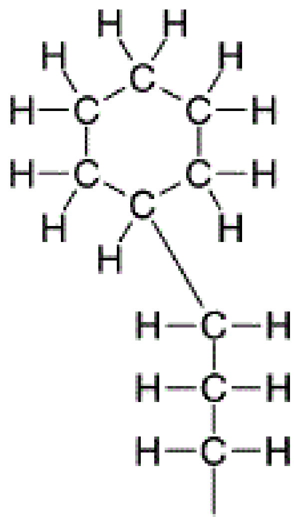
(non-polar)

How do detergents and dispersants work?

Hydrocarbons from petroleum

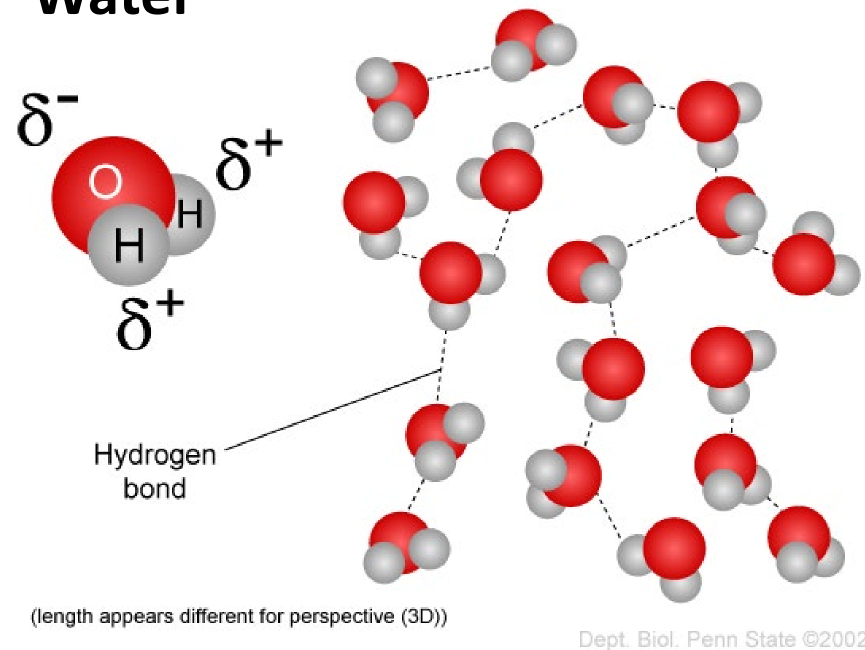


a) Paraffins

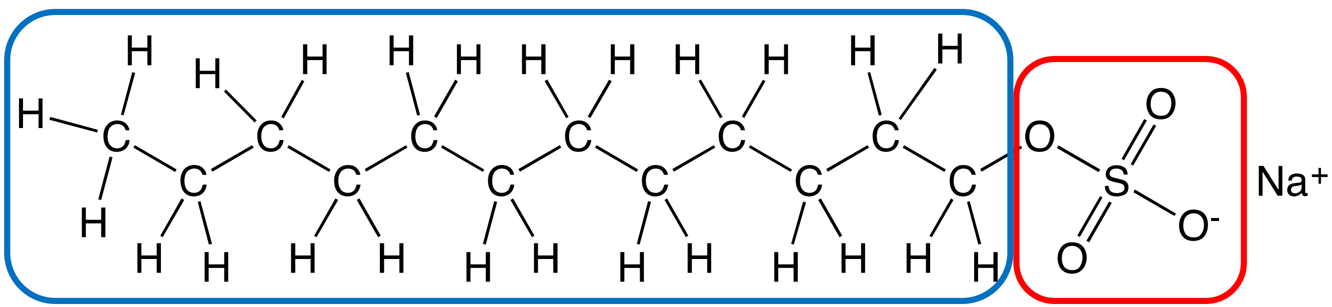


b) Naphthenes

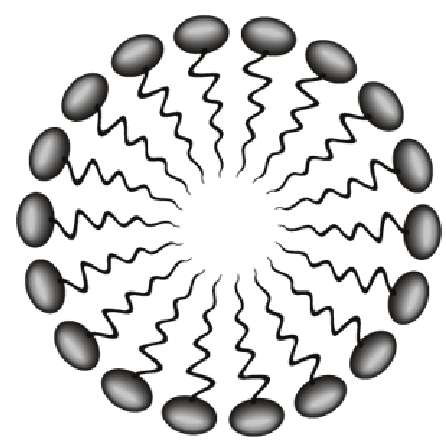
Water



(length appears different for perspective (3D))



sodium dodecyl sulfate



Detergent or dispersant