Chapter 9

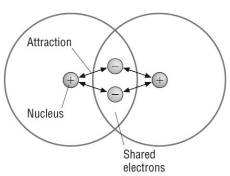
Molecular Compounds
&
Covalent Bonding

9.1 Why do covalent bonds form?

- If only the nonmetals in groups 5A, 6A, & 7A existed, ionic bonds couldn't form.
- The atoms in those groups need electrons so they are not willing to lose any.
- If two Hydrogen atoms are locked in a room together, how would they become stable?

What is a Covalent Bond

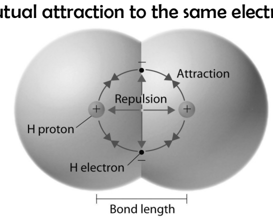
- The sharing of valence electrons between two nonmetal atoms
- There is no transfer of electrons because there are no metals present to lose electrons.

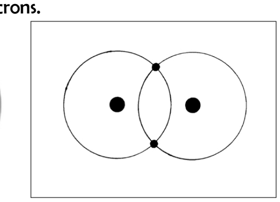


Keep in mind, there are attractive and repulsive forces in a covalent bond. The nuclei are attracted to the electrons, but are still repelling one another.

Formation of Covalent Bonds

Atoms overcome the nucleus' repulsive forces due to their mutual attraction to the same electrons.





What is a Molecule?

- Neutral group of atoms joined together by covalent bonds.
- Several atoms and several covalent bonds can be present in a molecule, unlike the formula unit of an ionic compound.
- Atoms are attached by more than just electrical attraction.

Diatomic Molecules

- a molecule consisting of two identical atoms
- There are 7: must memorize *(Hint: Starts at 7, makes a 7)*
  - H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2
- These are elemental compounds that are more stable as a compound than by themselves.

Molecular Formula

C_4H_6

Chemical formula for molecular compounds.

Shows the type of atoms and the the number of atoms.

Subscripts are not always in lowest whole number ratio.

- *Ionic compounds are in lowest whole number ratio called formula units.*

Does not give the structure or shape of the molecule

Properties of Molecular Compounds

- Lower melting and boiling points than ionic compounds.
- Most are gases or liquids at room temperature.
- Poor conductors of electricity
- Why do you think they possess these properties?

Ionic vs. Covalent

Formula Unit	Molecule
Transfer electrons	Share electrons
Metal - Nonmetal	Nonmetal-Nonmetal
Solid Crystals	Solid, liquid, gas
Good electrical conductor	Poor electrical conductor
High melting point	Low melting point

Gilbert Lewis Stated

- Sharing of electrons occurs if the atoms involved acquire the electron configurations of noble gases.
- Stable by sharing instead of losing or gaining electrons.
- Unpaired vs. Paired Electrons are significant in bonding

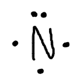
Element	Electron Distribution (Show Boxes)	Dot Structure	Electrons needed	Unpaired Eelctrons
Oxygen	$1s^2$ $2s^2 2p^4$ $\square - \square\square\square$			
Nitrogen	$1s^2$ $2s^2 2p^3$ $\square - \square\square\square$			
Carbon	$1s^2$ $2s^2 2p^2$ $\square - \square\square\square$			
Carbon	$1s^2$ $2s^1 2p^3$ $\square - \square\square\square$			

Carbon's Dot Structure Unique

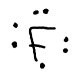
- It is slightly different when 2 carbon atoms form covalent bonds.
- A covalent bond is formed by the unpaired electrons of two atoms, but Carbon only has 2 unpaired electrons
- Carbon needs 4 more electrons, so it needs 4 unpaired electrons.
- $1s^2 2s^1 2p^3$, not $1s^2 2s^2 2p^2$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ $\boxed{\uparrow\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

Bonding Rules

Nitrogen: 3 unpaired electrons
needs 3 electrons to be stable
must form 3 covalent bonds

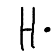


Fluorine: 1 unpaired electron
needs 1 electron to be stable
must form 1 covalent bond

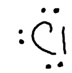


Bonding Rules

Hydrogen: 1 unpaired electron
needs 1 electron to be stable
must form 1 covalent bond

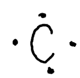


Chlorine: 1 unpaired electrons
needs 1 electron to be stable
must form 1 covalent bonds



Bonding Rules

Carbon: 4 unpaired electrons
needs 4 electrons to be stable
must form 4 covalent bonds



Oxygen: 2 unpaired electrons
needs 2 electrons to be stable
must form 2 covalent bonds

Unshared Pairs

- The pairs of valence electrons that are not shared between atoms are called unshared pairs of electrons, or unshared pairs.
- They are also called lone pairs or nonbonding pairs.
- These are extremely important in determining the shapes of molecules, never leave them out.

Single Covalent Bonds

Two valence electrons are being shared be two atoms.

H_2

Cl_2

More Single Covalent Bonds

H_2O

CH_4

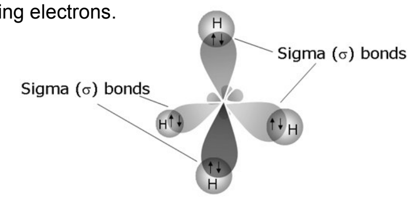
Sigma Bonds

Single Covalent Bonds (Greek letter: σ)

- When electrons are shared, the valence orbitals of one atom overlap the valence orbital of the other atom. *(Strong bonds)*
- The bonding orbital is the region between the two atoms in which the shared electrons are likely to be found.
- Can be s/s, s/p, or p/p orbitals overlapping.
- The bond is being pulled straight toward the central atom.

Images of Sigma Bonds

The sigma bond is the area centered between the two atoms that are sharing electrons.



Multiple Covalent Bonds

More than two valence electrons are being shared be two atoms.

O_2	N_2

Multiple Covalent Bonds

Single bond	Double bond	Triple bond
H–H	O=O	N≡N
H:H	·Ö::Ö·	N⋮N

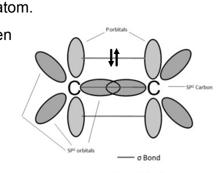
More Multiple Covalent Bonds

H_2O	CH_4

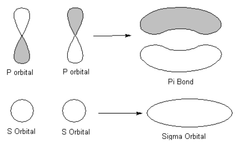
Pi Bonds

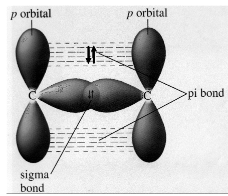
Parellel Orbitals overlap (Greek letter: π)

- Sideways overlapping, which means the shared electrons are not being pulled toward the central atom.
- A Pi bond always accompanies a sigma bond when forming double and triple covalent bonds.
- Formed only by p orbitals *(Weak bonds)*
- Remember, p orbitals are dumbell shaped, which makes them different



Sigma vs. Pi Bonds

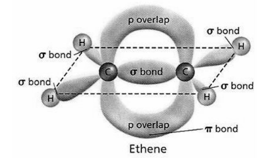


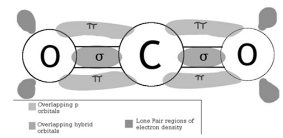


Images of Pi Bonds

The shared electron pair of the Pi bond occupies the space above and below the line where the atoms are joined.

- Image looks like there is 2 pi bonds, but it is one large pi bond.





Strength of Covalent Bonds

- Several factors control the strength of covalent bonds.
  - > Remember: the nuclei of bonded atoms are attracted to each other's electrons but repelling their nuclei.
- **Bond Length** is the most important factor: the distance that separates the bonded nuclei. *(Shorter is stronger)*
  - > Bond length decreases with more shared electrons.
  - > Triple bonds are strongest, single bonds are weakest.

Bond Dissociation Energy

The amount of energy required to break a covalent bond, It is different for all compounds.

In a chemical reaction, bonds are broken and formed.

- **Endothermic**: reactions in which more energy is required to break the bonds of the reactants than is released when bonds form.
- **Exothermic**: reactions in which more energy is released forming new bonds than is required to break the bonds of the reactants.

9.3 Molecular Structures

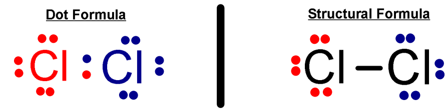
Lewis Dot Formulas: show which atoms are pairing up to form bonds

Structural formulas: show the arrangement of atoms in molecules and polyatomic ions.

Dashes are used in structural formulas

- 1 dash: 2 shared electrons
- 2 dashes: 4 shared electrons
- 3 dashes: 6 shared electrons

Dot Formula | **Structural Formula**



How many electrons are donated by each chlorine? _____

How many unshared pairs are in the molecule? _____

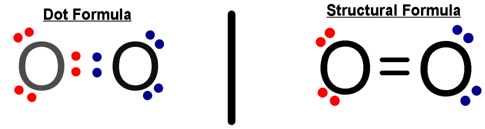
How many electrons are being shared? _____

How many shared pairs are in the molecule?_____

Double and Triple Covalent Bonds

- Double covalent bonds involve two shared pairs of electrons.
  - > Represented by 2 dashes
- Triple covalent bonds involve three shared pairs of electrons.
  - > Represented by 3 dashes

Dot Formula | Structural Formula



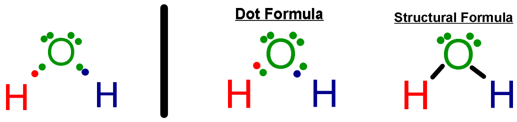
How many electrons are donated by each oxygen? _____

How many unshared pairs are in the molecule? _____

How many electrons are being shared? _____

How many shared pairs are in the molecule?_____

Dot Formula | Structural Formula



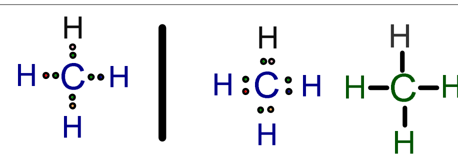
How many electrons are donated by each hydrogen? _____

How many electrons are donated by the oxygen? _____

How many unshared pairs are in the molecule? _____

How many electrons are being shared? _____

How many shared pairs are in the molecule?_____



How many electrons are donated by each hydrogen? _____

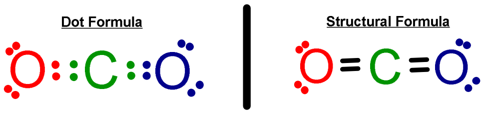
How many electrons are donated by the carbon?_____

How many unshared pairs are in the molecule? _____

How many electrons are being shared? _____

How many shared pairs are in the molecule?_____

Dot Formula | Structural Formula



How many electrons are donated by each oxygen? _____

How many electrons are donated by the carbon?_____

How many unshared pairs are in the molecule? _____

How many electrons are being shared? _____

How many shared pairs are in the molecule?_____

C_2H_4

Lewis Formula | Structural Formula

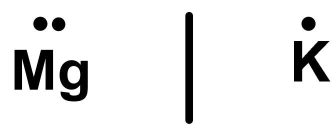
C_2H_6O	$C_4H_6O_2$

Why don’t metals usually form covalent bonds?

Mg has 2 valence electrons.
- How many covalent bonds must it form to be stable?
- How many electrons does it have to donate?

- How about Aluminum?

Why don't metals form covalent bonds?



How many more electrons does each atom need to be stable?______

How many covalent bonds can each atom form?______

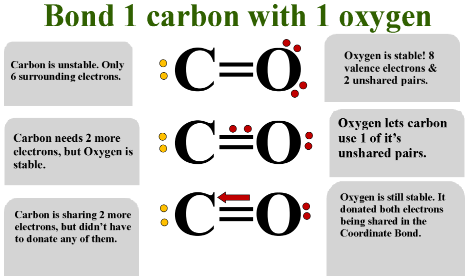
Coordinate Covalent Bonds

Emergency Bonds

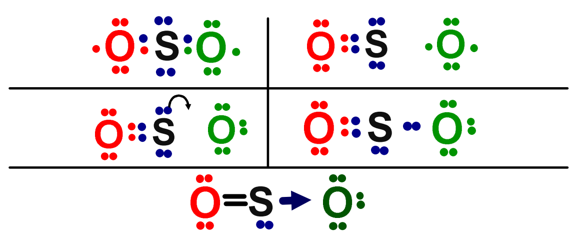
A coordinate covalent bond is formed when one atom contributes both bonding electrons in a covalent bond.

- Once formed, they act as normal covalent bonds.
- Electrons are mobile, which allows them to be “fluid”
- Used in Polyatomic ion formation
- Arrows are used to indicate a coordinate covalent bond
- Ex.) CO, NH_4^+, H_3O^+, SO_3, SO_4^{2-}

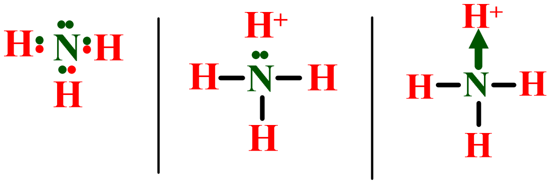
Bond 1 carbon with 1 oxygen



Coordinate Covalent Bonds SO_2

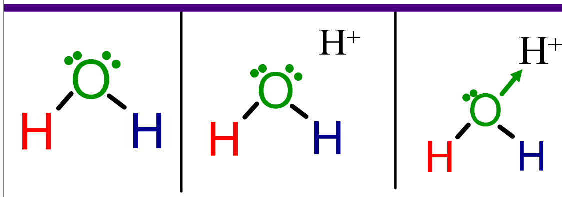


NH_4^+

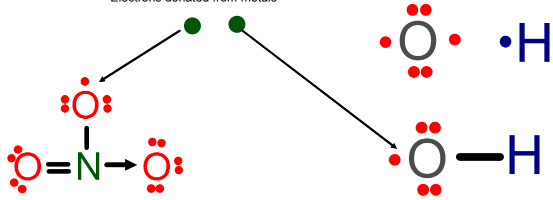


The unshared pair is now a bond, not an unshared pair.

H_3O^+

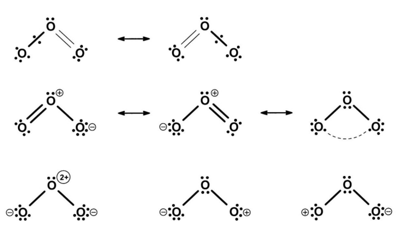


Negative Polyatomic Ions



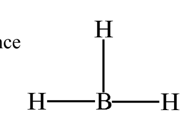
Resonance

- Resonance structures occur when two or more valid electron dot formulas can be written for a molecule.
- Differ in the position of the electron pairs, not the position of the atoms.
- Ex. O_3, CO_3^{2-}
- Same formula but different structure due to the locations of the electron pairs.

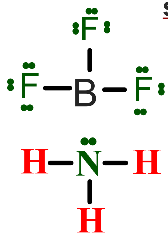


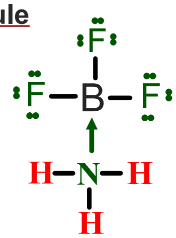
Exceptions to the Octet Rule

- Sometimes it is impossible to write electron dot structures that fulfill the octet rule.
- Occurs whenever the total number of valence electrons in the species is an odd number.
- Only certain substances can form covalent bonds and have less that 8 valence electrons.
- Boron can only form 3 bonds.



May use a coordinate covalent bond to satisfy octet rule

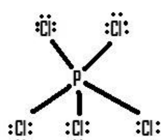


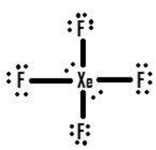


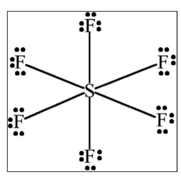
Expanding the Octet

- when atoms are surrounded by more than 8 electrons
- Some atoms have empty "d" orbitals that can be used to hold extra electrons.
- Electrons from an unshared pair move into the "d" orbitals so they can become unpaired electrons, which can bond.

Ex.) PCl_5, SF_6, XeF_4







9.4 Molecular Shape

- VSEPR theory states that because electron pairs repel, molecules adjust their shapes so that the valence-electron pairs are as far apart as possible.
- **V**alence **S**hell **E**lectron **P**air **R**epulsion.
- Bond angles are created by this repulsion of electrons

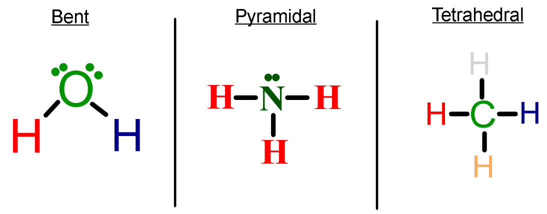
More about shapes…

- Molecules are 3 dimensional.
- Molecular shape is determined by the number of bonds formed and by the unshared pairs of electrons.
- Each shape has a specific bond angle.

Bond Angles

- Tetrahedral = 109.5° *(sp^3 hybridization)*
- Linear = 180° *(sp hybridization)*
- Bent = 104.5° *(sp^3 hybridization)*
- Tigonal Pyramidal = 107.3° *(sp^3 hybridization)*
- Trigonal Planar = 120° *(sp^2 hybridization)*

Molecular Shapes



Hybridization in Molecules

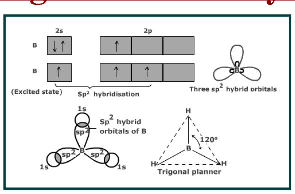
Occurs in atomic orbitals during bonding.

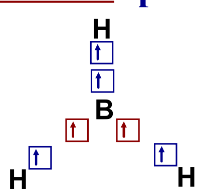
Hybrid = two different types of orbitals are involved.

Shows which orbitals of a bonded atom have paired electrons.

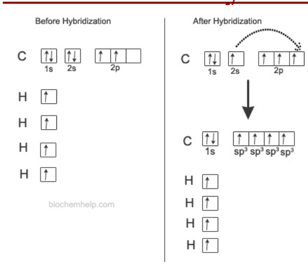
- Hybrid orbitals can be occupied by a shared pair of electrons or an unshared pair of electrons. *(aka: Lone pairs)*

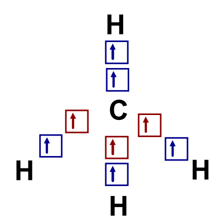
Trigonal Planar Hybridization sp2



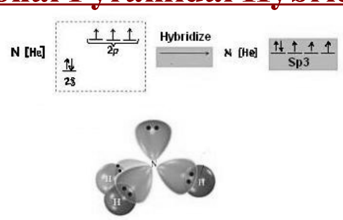


Tetrahedral Hybridization sp^3





Trigonal Pyramidal Hybridization



Sp^3 hybridization in NH_3

Common Molecular Shapes

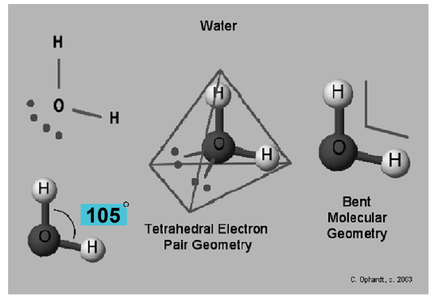
Linear: HCN, CO_2
All binary compounds
2 Bonds & 0 unshared pairs
No unshared pairs on central atom to bend molecule

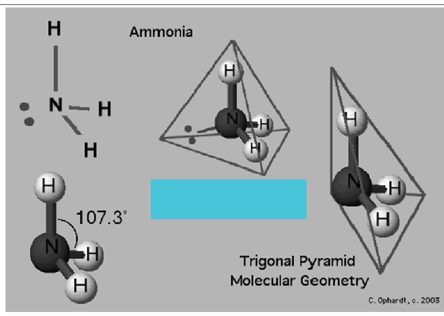
Trigonal Planar: BH_3, COH_2
3 bonds & 0 unshared pair

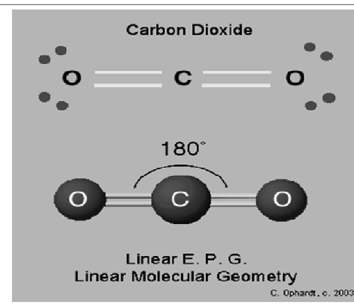
Bent triatomic: H_2O
2 bonds & 2 unshared pair
Unshared pairs bend the molecule
2 unshared pair is bent most

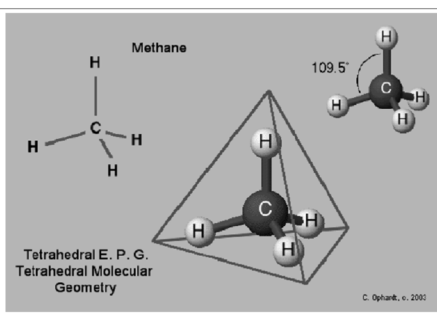
Trigonal Pyramidal: NH_3, H_3O^+
3 bonds & 1 unshared pair

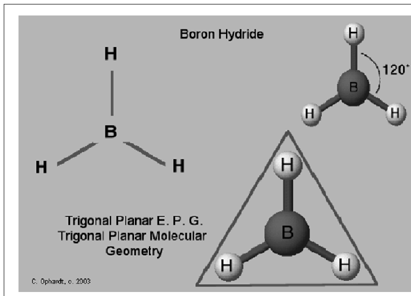
Tetrahedral: CH_4, CCl_4, NH_4^+
4 bonds & 0 unshared pair











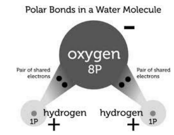
9.5 Electronegativity and Polarity

- Ability of atoms to attract electrons.
- Determines the reactivity and strength of polar covalent bonds.

F = 4.0	Br = 2.8
O = 3.5	I = 2.5
N = 3.0	C = 2.5
Cl = 3.0	S = 2.5
Hydrogen = 2.1	

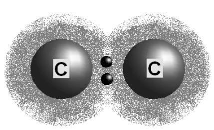
Polar Covalent Bonds

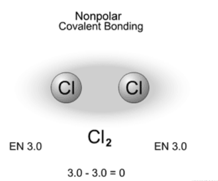
- When two different atoms are joined by a covalent bond and the bonding electrons are shared unequally
- The atom with stronger electronegativity in a polar bond acquires a slightly negative charge. The less electronegative atom acquires a slightly positive charge.
- HCl: Moderately polar covalent
- HF: Very polar covalent (Reactive)



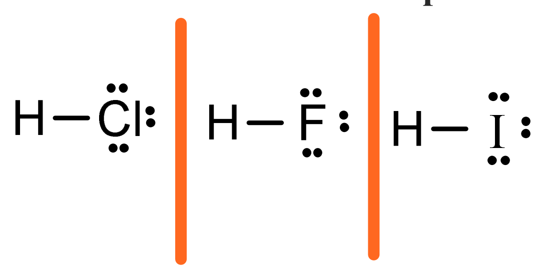
Nonpolar Covalent Bonds

- When the atoms in a bond are the same, the bonding electrons are shared equally
- Ex. diatomics





Which bond is the most polar?



Dipolar Molecules

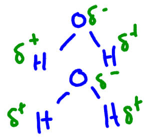
- In a polar molecule one end of the molecule is slightly negative and the other is slightly positive.
- Dipolar molecules (2 poles)
- Not every molecule with polar bonds is dipolar.
- Ionic compounds are soluble in polar molecules.
- Ex.) HCl, H_2O, HF

Nonpolar Molecules

- When a molecule has no difference in charge between opposite ends or sides of the molecule.
- Not very reactive since they are not dipolar
- **H_2, F_2, CO_2, Cl_2, CCl_4**
- Water is only polar due to it's shape

Attractions Between Molecules

- In addition to covalent bonds in molecules, there are attractions between molecules, or intermolecular attractions
- Covalently bonded atoms attracted to each other.



Gases	Liquids	Solids
No attraction	Dipole Attraction	Ionic Attraction
Nonpolar Molecules	Polar Molecules	Ions Form Crystals

Intermolecular Attractions (Between)

These are what hold molecules together.

- Weaker than either an ionic or covalent bond.
- They are responsible for whether a molecular compound is a gas, liquid, or solid.

Van der Waals forces

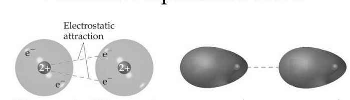
- The weakest attractions between molecules. **Not Bonds!!!!!!**
- Three types are Dispersion forces, Dipole interations, and Hydrogen bonds
- Hydrogen > Dipole > Dispersion

Attractions between polarized molecules

Dispersion Forces

- The weakest of all intermolecular interactions.
- Thought to be caused by the motion of electrons, and remember, electrons are always moving.
- Strength of dispersion forces increases as the number of electrons in a molecule increases
- Electrons are not lost or gained

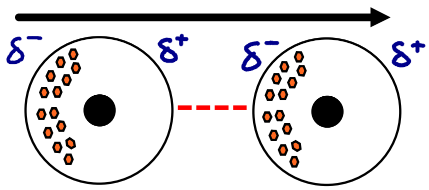
London Dispersion Forces



London dispersion forces are attractions between an instantaneous dipole and an induced dipole.

Dispersion forces

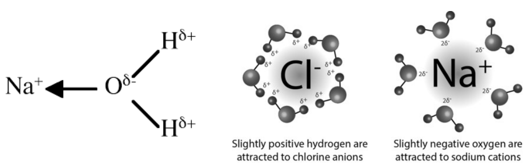
Due to movement, the electrons move to one side and create a separation of charge.



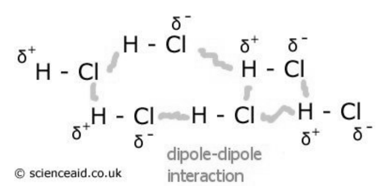
Dipole Interactions

- Occur when polar molecules are attracted to one another
- Electrostatic attractions occur between the oppositely charged regions of dipolar molecules.
- Similar to ionic bonding, but much weaker attraction.

Ion - Dipole Interactions



Dipole - Dipole Interactions



Hydrogen Bonds

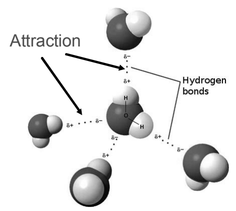
- Strongest of all intermolecular attractions. *Must involve hydrogen*!
- Dipole interactions with hydrogen.
- An atom or molecule is attracted to a Hydrogen atom that is already bonded to an atom with high electronegativity.
- The covalently bonded hydrogen becomes slightly positive.
- Unshared electron pairs and atoms with high electronegativity become attracted to the slightly(+) Hydrogen.

Why is there so much water?

Water molecules are polar.

- The oxygen atom becomes slightly negative and each hydrogen becomes slightly positive.
- This causes an intermolecular attraction between water molecules.
- The attraction water molecules have for one another is called Hydrogen bonding.

Hydrogen Bonding in Water



Hydrogen Bonding is the attraction between polar molecules with hydrogen.

Properties of Molecular Substances

- The physical properties of a compound depend on the type of bonding it displays.
- Ionic or Covalent

Network Solid

- All of the atoms are covalently bonded to each other. *(Crystals)*
- No intermolecular attractions.
- Most stable type of molecule.
- Very high melting point.
- Ex.) Diamonds

Network Solid Image