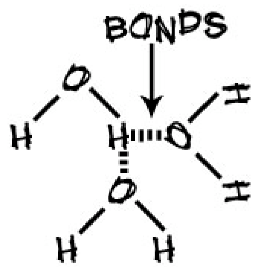
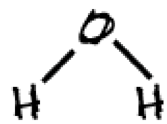
2/27/06 – 3/1/06

Non-Covalent Molecular Forces

How does this reaction occur: H_2O (liquid) → H_2O (gas) ?



Add **energy** →



H_2O gas: molecules are very far apart

H_2O liquid: bonding between molecules

- Use **heat** to add energy. i.e. boil water to turn H_2O to gas

- Boiling point
    - How much energy do you need to change a substance from liquid to gas state?
    - Water's boiling point is *high* for a molecule weighing only 18amu. Why?

Data	Boiling Point
NaCl	1413 ºC
BrCl	5 ºC
H_2O	100 ºC
Ar	- 186 ºC

Ionic: NaCl

Is it **Na—Cl** or **$Na^+ Cl^-$** ?
Covalent? Ionic?

ΔEN (change in electronegativity) ~ 1.6 +

- ΔEN = 3.0 (Chlorine) – 0.9 (Sodium) = 2.1 → **ionic**

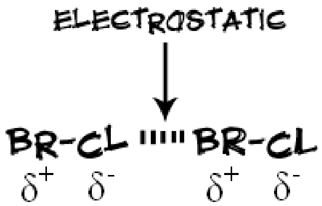
- Ionic → Strong bond
    - The negative ion of chlorine is electro-statically attracted to the positive charge on sodium
    - 188 kcal/mol to break the bond. Huge number, but typical for ionic compounds.
    - **Therefore, NaCl's boiling point is high (1413 ºC)** because it takes a lot of energy (in the form of heat, in this case) to break the bonds and turn the molecule into its gas state

Dipole-Dipole: BrCl

Is it **Br—Cl** **or** **$Br^+ Cl^-$?**

- ΔEN = 3.0 (Chlorine) – 2.8 (Bromine) = 0.2 → **covalent?**

- → Sharing of electrons not *completely* even and covalent, so BrCl is best described as **polar covalent.**



Polar Covalent

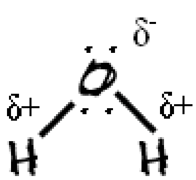
Electrostatic Attraction = opposite charges that attract bonds and have permanent dipoles, dipole-dipole bonding.

(Strength of attraction follows Coulomb's Law: force of electrostatic attraction is proportional to magnitude of the difference between charges)

- One BrCl molecule has a covalent bond where chlorine is more electronegative (electron-greedy) than bromine. This causes a shift in electron density towards chlorine, resulting in a slight negative dipole. Thus bromine obtains a slight positive dipole because it is lacking electron density.
    - The negative dipole from the chlorine of one BrCl molecule then becomes attracted to the positive dipole from a bromine atom of a different BrCl molecule (opposite charges attract!).
        - → **Dipole-dipole attraction** accounts for BrCl's 5 ºC boiling point
- In ionic case, force of attraction is stronger and bonds are harder to break compared to dipole-dipole (_$^+$, _$^-$) attraction.
- Bond dipole depends on:
  → ΔEN
  → bond length

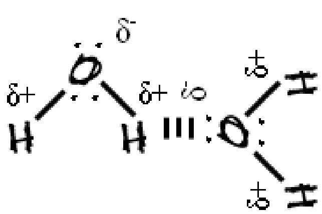
  Examples:
  Br—Cl ΔEN = 0.2
  H_3C—H ΔEN = 0.4 (bond is *shorter*)

Hydrogen Bonding: H_2O



- Ionic? ΔEN = 3.5 (oxygen) – 2.1 (hydrogen) = 1.4
    - → Borderline value, but more *covalent* than ionic

- Dipole-dipole interaction between two molecules? Yes!

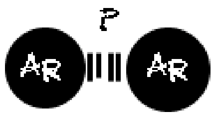


← **Hydrogen bonding** between the negative dipole of oxygen and the positive dipole of the hydrogen of a *different* molecule. This reaction is very important and very widespread.

- **Hydrogen bonding** requires a hydrogen with a large positive dipole (resulting from a hydrogen attached to a very electronegative atom) and another acceptor atom with a very negative dipole (i.e. a negatively charged atom) or a neutral oxygen or nitrogen with lone pairs.

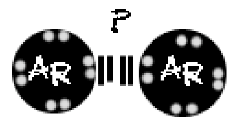
Van der Waals: Argon

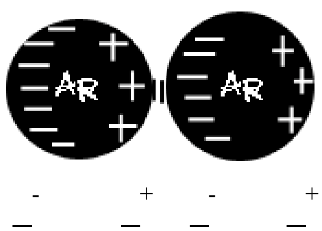
- Ar has a boiling point, there must be some force acting between molecules:
  - **Ionic?** No! There is no difference in electronegativity between two argons.
  - **Dipole—dipole?** No! No bonds, no dipoles.
  - **H-bonded?** No hydrogen!
  - **Then what?**



What force is holding these atoms at all? There's a boiling point above absolute zero, so there must be some force.

Electrons can respond quickly and move faster than nuclei. Two argon atoms normally don't "like" each other because they both have full shells.





← Electrons can shift to one side. Now they like each other! *Attractive force* is present, weak, and temporary. It is (1) fleeting and (2) a contact force. Two atoms must be close together in order to distort their electron clouds and result in this attractive force.

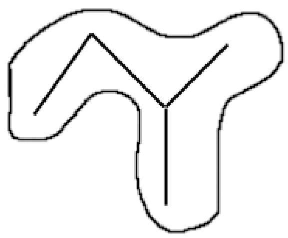
- The attractive force is called: "London dispersion" a.k.a. **<u>"Van der Waals"</u>** forces.
  - What do you need for this force to be present?
    - Electrons (an electron cloud). That's ALL you need!
    - Therefore: every molecule is influenced by this force
    - The extent to which the force is present depends on how easy it is to move (distort) the electron clouds.
      - i.e. **polarizability.**
      - Van der Waals strength:
        - easily distorted clouds are called "**soft**"
        - difficult to distort clouds are called "**hard**"

Atom	Boiling Point (ºC)	Trends	
He	- 269	Harder	Smallest atom, low atomic weight
Ne	- 246	|	
Ar	- 189	|	
Kr	- 152	|	
Xe	- 107	V	
Rn	- 62	Softer	Largest atom, highest atomic weight

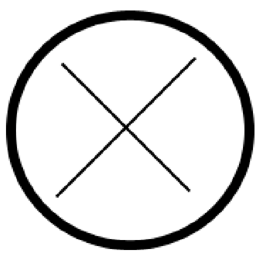
- Why is it easier to distort Radon (Rn)? It's larger.
  - In Rn, its valence electrons are further apart because it is a bigger atom. Therefore the nucleus has less control over the electrons and Rn is *softer*
- **Trend: atomic weight**
  - General, broad rule, but weight is not exactly a true trend.

Boiling point = 36 ºC

Sausage-shaped, more surface area.



Boiling point = 30 ºC



Boiling point = 9.5 ºC

~ Sphere shape: less surface area

- **Trend: boiling point *decreases* with *more branches and less surface area*.** This means that Van der Waals forces are stronger when the molecule has greater surface area.

- **Van der Waals is dependent on:**
  - Polarizability (hard/soft)
  - Surface area (the more SA, stronger Van der Waals force)

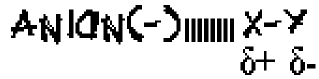
<u>Relative Strength</u>

1.	Ionic strength	= hundreds of kcal/mol
2.	Covalent bonds	= 30-160 kcal/mol
3.	Dipole-dipole	= ~ tens of kcal/mol
4.	H-bonding	= ~ 5 kcal/ mol
5.	Van der Waals	= 0-1 kcal/mol

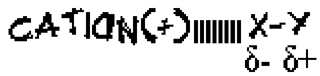
<u>Other non-covalent forces:</u>

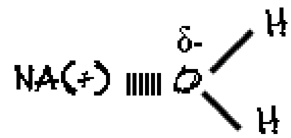
A) Ion—dipole

- A bond dipole interacts with an ion
  1. A negative ion (anion) is attracted to a positive dipole of another molecule.
  2. A positive ion (cation) attracts the negative dipole of another molecule.

Example i. 

A chlorine ion (-) is attracted to the positive dipole of hydrogen in a water molecule.

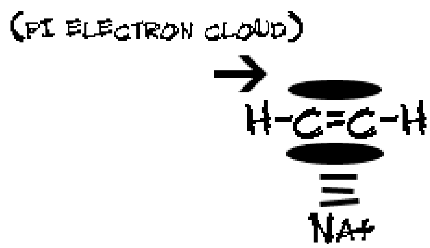
Example ii. 



A sodium ion (+) is attracted to the negative dipole of an oxygen in a water molecule.

B) Ion—pi

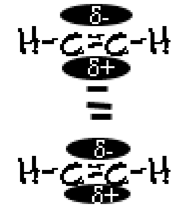
- The pi electron cloud of a molecule with a pi bond is attracted to a positive ion (cation)
- i.e., the double bond in benzene produce pi electron clouds that attract cations.



C) Pi stacking

- An attraction that occurs when two pi electron clouds of different molecules become distorted (like in Van der Waals forces) and result in a weak attraction.
- i.e. two benzene rings.
    - **i.** When the pi electron cloud of one benzene ring becomes attracted to that of another, its electrons shift away from the other molecule (negative charges repel each other)
        - This results in a *positive dipole* on one side of the pi electron cloud, which subsequently attracts the electrons of the second benzene, which shift towards the positive dipole.

Ex: two benzenes
The electrons of the first benzene shift away from the second benzene.
This creates a new dipole, which attracts the electron cloud
from the pi bond of the second benzene. A pi stacking attractive force is formed.



Consequences: Solubility

What do noncovalent forces influence?

- **<u>Solubility</u>** – do two things dissolve in each other?
  - For dissolving to occur, new solution must be more stable than the individual components (the nondissolved, heterogenous molecules)
  - For example, take two separate, heterogenous, non-dissolved solutions containing either molecules A or molecules B
    - A and B have to offer more to each other than A offers to A or B offers to B.
    - For A to dissolve in B, A must disrupt the attractive forces holding the B molecules together

The new solution must offer enough stabilization to overcome forces keeping the solute in a solid state. i.e. NaCl and water (example below).

<u>Example 1:</u>

The equilibrium reaction: $NaCl + H_2O$ _ $Na^+(aq) + Cl^-(aq)$

- Salt dissolves readily and water, so the right side of the equilibrium should be favored
- What forces keep NaCl together? IONIC (strong forces!)
- What forces hold water together? Hydrogen bonding and dipole-dipole

What does sodium gain from being aqueous?

- Water represents a source of electron density to sodium, Na^+
  - Water has *extra* electron density in its lone pairs and has a negative dipole
  - An ion-dipole force draws the positive Na^+ ion and the negative dipole of an oxygen atom in water molecule together

What does chlorine gain from being aqueous?

- Chlorine has excess electron density and is looking for something electron deficient.
  - The hydrogens in water have a strong positive dipole
  - A hydrogen bond is formed between the negative ion Cl^- and a hydrogen of a water molecule

- Why does NaCl give up its strong ionic attraction for the weak ion-dipole and hydrogen bonding it gains from water?
  - **<u>QUANTITY</u>** wins over **quality**
  - Dissolved NaCl has a larger volume than solid NaCl
  - The ionic forces in solid NaCl are strong, but this does not win over quantity.

<u>Example 2:</u>

- Italian dressing is oil (a hydrocarbon) and vinegar (H_2O + acetic acid)
  - When you let the dressing sit, the oil *always* separates from the vinegar
- It is hard to dissolve anything in oil. Why?
  - There are no large dipole-dipole interactions in oil
  - Van der Waals forces are the only noncovalent molecular forces present, which are very weak and fleeting. Water doesn't dissolve in oil because it is not attractive (what can oil offer water? Weak Van der Waals forces aren't good enough.)

- It makes sense that polar dissolves in polar, but in some instances, polar *can* dissolve in nonpolar!