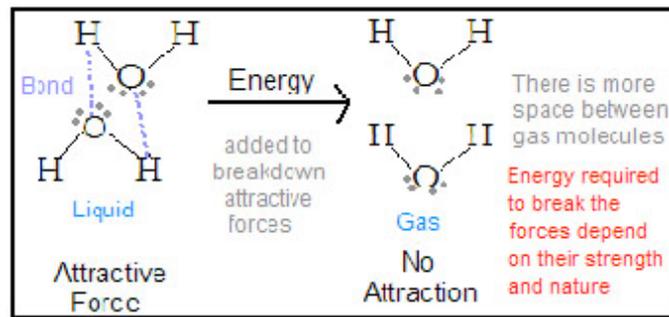


INTERMOLECULAR FORCES

Intermolecular forces- forces of attraction and repulsion **between** molecules that hold molecules, ions, and atoms together.

Intramolecular - forces of chemical bonds **within** a molecule



Boiling Point and Electronegativity

Boiling Point

- the temperature at which the liquid form of a compound vaporizes into a gas.
- the attractive forces in the liquid must be overcome to become a gas.
- boiling point of 0 = no attractive force

Trends:

Compound	Boiling Point
NaCl	1413 C
BrCl	5 C
H ₂ O	100 C
Ar	-186 C

↑
Increasing
Attractive
Forces
↑
Increasing
Boiling
Point

Boiling Point example from Bruice 5.2

Explain trend in boiling points of H Halides: HCl, -85°C; HBr, -67°C; HI, -15°C

Answer:

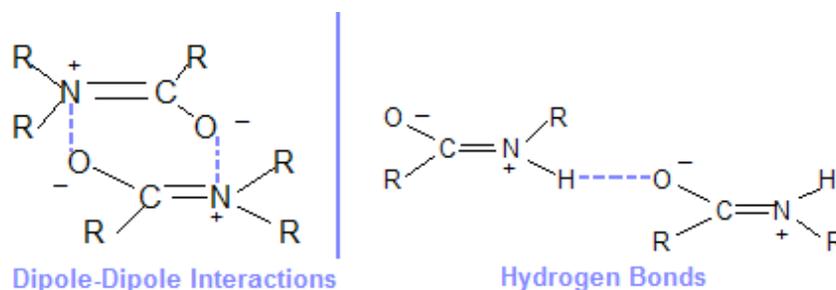
Stronger intermolecular forces result in higher boiling points. The dipole moments increase with the polarity of the H-X bond (the greater the difference in EN between the H and halogen atoms, the stronger the dipole-dipole attractions.) The strength of London forces increases with the number of electrons

Cl is more EN than I so HCl should have a greater boiling point but this data suggests that **London forces dominate dipole-dipole interactions** for these molecules since Iodine is larger than Cl.

Relative Boiling Points

amide > carboxylic acid > nitrile >> Ester ~acyl chloride ~aldehyde~ ketone

Amides have highest boiling points because they have strong dipole-dipole interactions because of resonance.



Electronegativity - the attractive force that an atom exerts on an electron (e⁻)

- closer e- to nucleus = more electronegative
- more protons, more positive, more attractive to e-

Electronegative difference:

- Ionic Bonds = >2.0
- Polar Covalent Bonds = 0.5 - 2.0
- Nonpolar Covalent Bonds (equal sharing of e-) = < 0.5

- **Electrostatic Attraction** (common in every noncovalent molecular force)= when opposite charges with permanent dipoles attract bonding

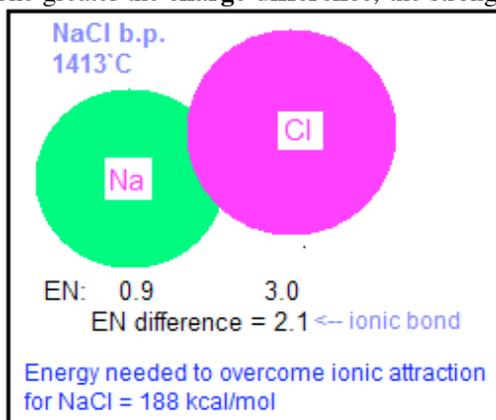
IONIC

Ionic Bond (strongest bond)

- a complete transfer of one or more e- occurs when one interacting atom is much more electronegative than the other.
 - one gives up e- (cation) and one takes e- (anion) making ions that are electrostatically attracted.
 - It takes a lot of energy to break ionic bonds and to turn the molecule into a gas

STRENGTH: strongest bond

TREND: The greater the **charge difference**, the stronger the attraction

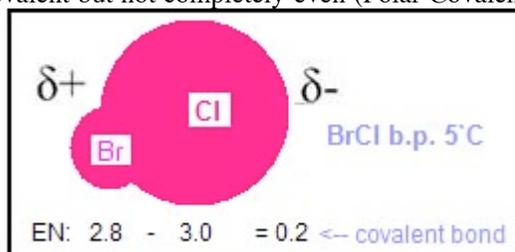


Coulomb's Law The repulsion force F is directly proportional to the product of the charges, $q_1 * q_2$

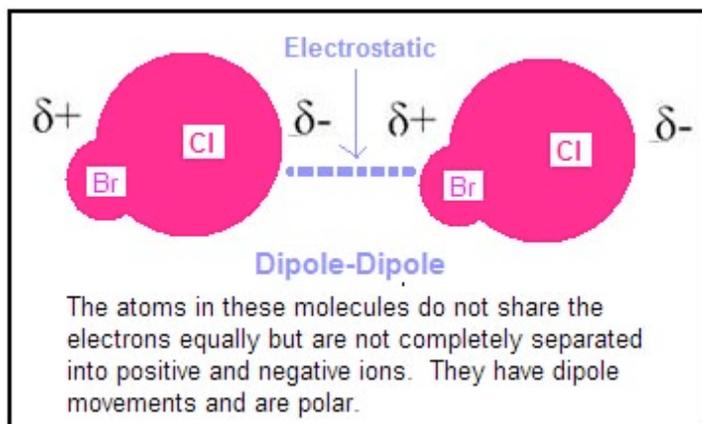
$$F_e \propto \frac{q_1 q_2}{r^2}$$

DIPOLE-DIPOLE

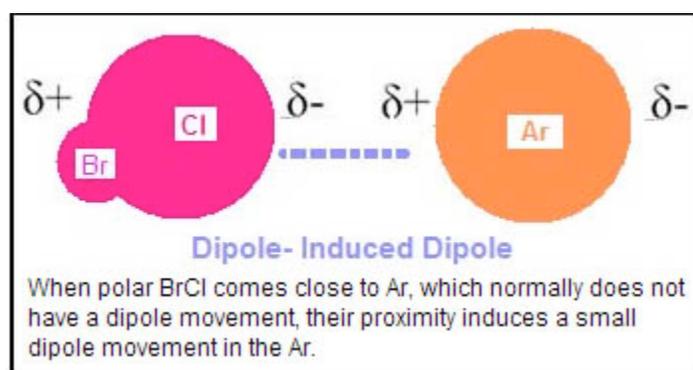
- sharing of electrons in a bond is covalent but not completely even (Polar Covalent)



- There is a polar covalent bond between the Br and Cl atoms. The electron density shifts towards chlorine since it is more electronegative than bromine. Chlorine thus has a slight negative dipole and bromine has a slight positive dipole.



- The negative dipole of the chlorine is attracted to the positive dipole of the bromine of another BrCl molecule. This dipole-dipole attraction accounts for the BrCl b.p. of 5°C



TRENDS:

- Electronegative Difference.** Polarity is amplified when electronegativity difference is large and minimized when the difference is small.
- Bond Length** (primarily atomic radii of the bonding partners)
 - Increasing bond length decreases dipole

HYDROGEN BONDING

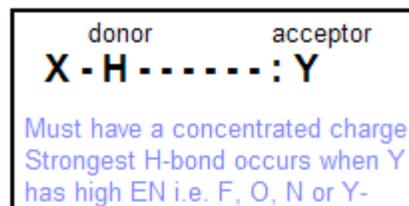
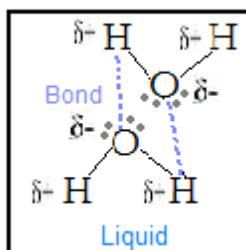
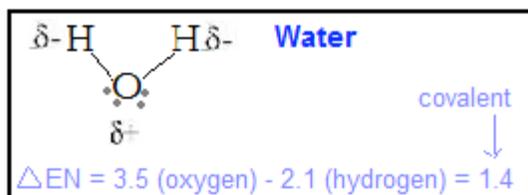
- A dipole-dipole interaction where the H atom is noncovalently attracted to an electronegative atom
- The H must have a large positive delta and the other atom must have a source of electrons to be attracted to H
- Usually negatively charged F, O, N is attracted to the positively charged H
- Very important biologically

STRENGTH:

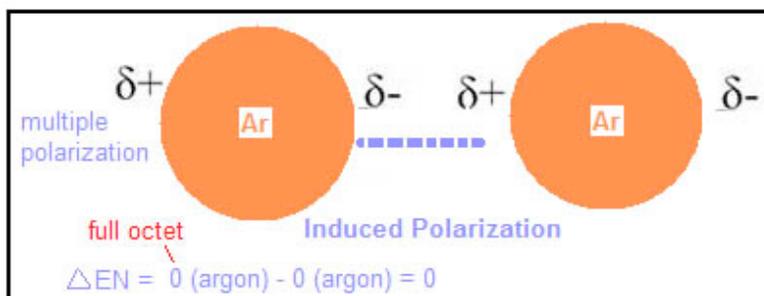
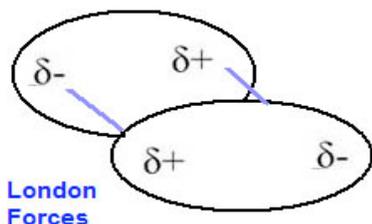
- a H bond is a weak bond and is dynamic [3×10^{-12} lifetime]
- In solid phase H-bond is static
- H-bonds between molecules continually form and break in liquid.
 - Every water molecule forms 3.4 H bonds with other water molecules

TREND:

- The **more electronegative** the atom attracted to H, the stronger the bond



LONDON / VAN DER WAALS FORCES



Principle : Electron can respond to changes must faster than nucleus

London Dispersion Forces/ Van der Waals Forces

- The attraction between instantaneous electric dipoles on adjacent molecules
- Present in all molecules because everything has an electron cloud

STRENGTH:

- Weak because temporary

TRENDS:

- Strength increases with # of electrons in molecule
- strength depends on the **polarizability** [ease with which their electron clouds can be distorted]
 - Molecules with lesser EN and larger radii have higher polarizability.
 - Higher polarizability = stronger attraction.

Atom	Boiling Point
He	-269°C
Ne	-246°C
Ar	-186°C
Kr	-152°C
Xe	-107°C
Rn	-62°C

As you travel down the periodic table

weakest attractive force

Increasing Boiling Point

strongest attractive force

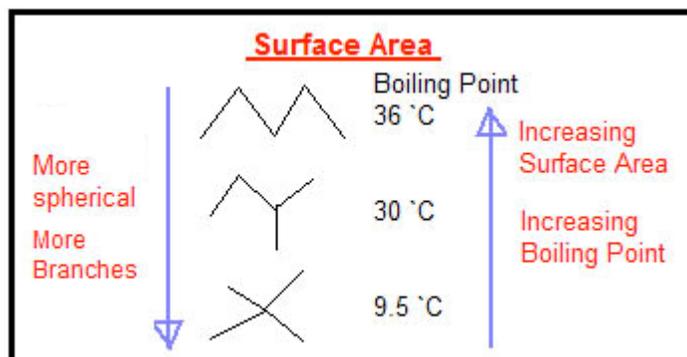
TRENDS:

1. The smaller the atom, the harder it is to distort the e- cloud (low polarizability) since the electrons are closer to the nucleus

The larger the atom, the easier it is to distort the e- cloud (high polarizability) because the valent electrons are further away from the nucleus and experience shielding from the nucleus' pull. [polarizability]

I.e. He is small, Rn is larger

2. Surface Area --- increasing surface area, increasing boiling point
3. Molecular/ Atomic weight --- increasing weight, increasing boiling point



Type of Interaction	Interacting Species
Ionic	Ions only
Dipole-Dipole	Polar Molecules (stationary ones have more energy than rotating ones)
Hydrogen Bonding	H-F, -O, -N
Van der Waals Forces	All Molecules (just need e- cloud)
Ion-Dipole	Ions & Polar Molecules
Cation-Pi	Pi-Electron Cloud & Cation
Pi Stacking	Two different Pi-Electron Clouds

RELATIVE ATTRACTION STRENGTHS	
Bond	Energy
Ionic	Hundreds of kcal/mol
(covalent)	40-160 kcal/mol
Dipole-Dipole	1-10 kcal/mol
H-bonding	1-10 kcal/mol
Van der Waals	0-1 kcal/mol

Increasing strength ↑

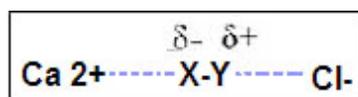
OTHER NON-COVALENT FORCES *all electrostatic in nature*

A) ION-DIPOLE

- An attraction that occurs when a dipole interacts with an ion
 - a negative ion attracts the positive dipole of another molecule
 - a positive ion attracts the negative dipole of another molecule

Strength: increases as ion charge or the dipole magnitude of the polar molecule increases.

Importance: Most commonly found in solutions and are especially important when dealing with solubility

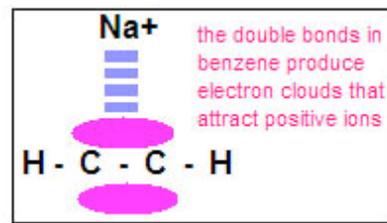


B) CATION - PI (side of benzene ring)

- A weak attraction that occurs between a cation and the electron-rich pi orbital of an aromatic ring

Strength: relatively strong, strength \sim H-bond

Importance: Important forces in protein



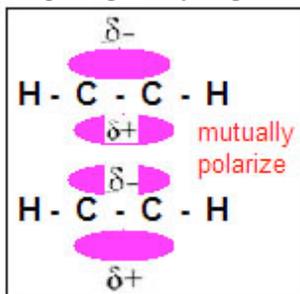
C) PI STACKING

- A weak attraction that results from the distortion of two different pi -electron clouds
- When the pi-electron cloud of one benzene ring becomes attracted to that of another, the negative dipoles repel each other so the electrons shift away from the other molecule. A positive dipole is created on the other side of the pi-electron cloud. The negative dipole movement of a second benzene ring is attracted to this induced positive dipole.

Strength: weak attraction

Importance:

- These attractions between nucleotides add extra stability to DNA
- Occurs most frequently with aromatic rings (especially important to enzymes)



CONSEQUENCES OF NON-COVALENT FORCES : SOLUBILITY

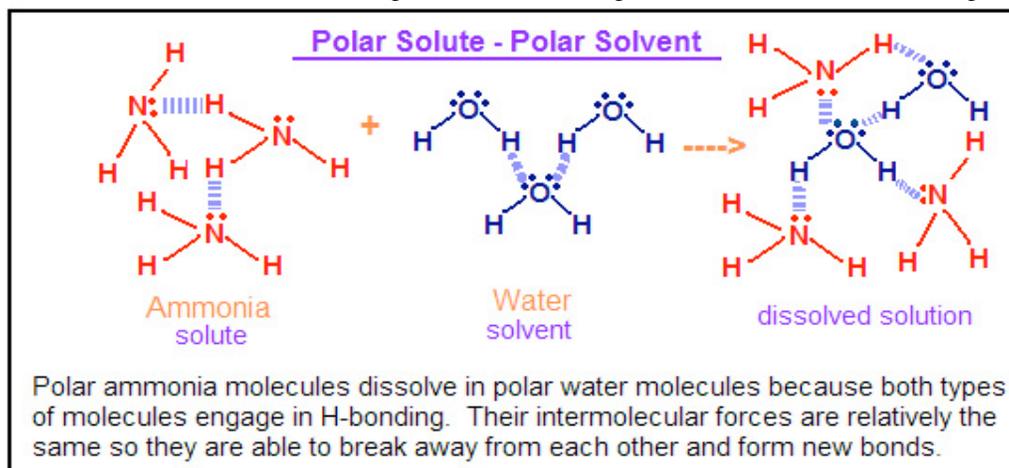
Solution:

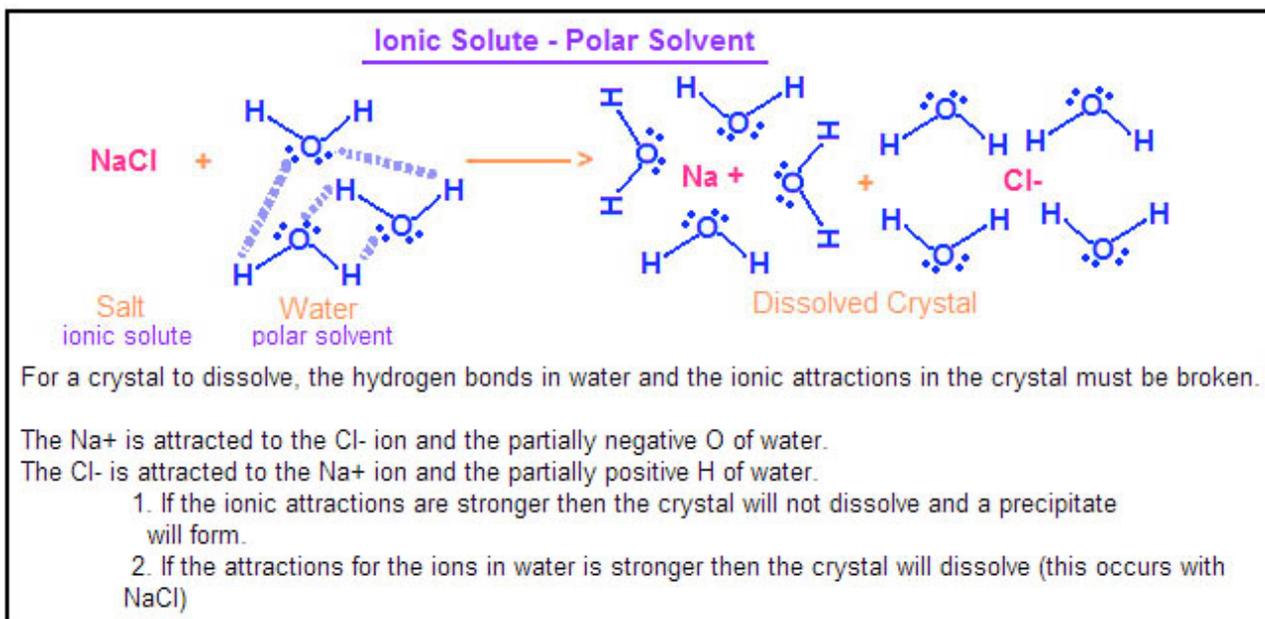
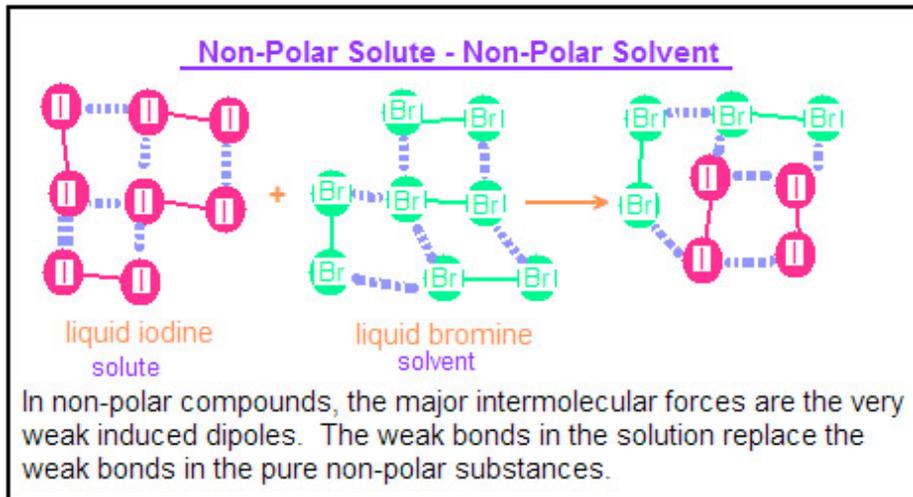
- mixture of two or more substances in a single phase.
- **solute** = a dissolvable substance that is available in the smallest amount
- **solvent** = the substance available in the larger amount (water most common)

Solubility:

- A solute will dissolve in a solvent if the solute-solvent attractive forces are great enough to overcome the attractive forces within the solute and the attractive forces within the solvent.
 - The solvent and solute will generally be soluble in each other if their forces are relatively equal.
 - A solute will only dissolve if the solute-solvent forces it will gain from being dissolved are stronger than the forces between solute-solute and the forces between solvent-solvent.
 - If the bonds are stronger in the solute-solvent forces, the substances will gain stability with the bonds achieved by dissolving and will readily dissolve.

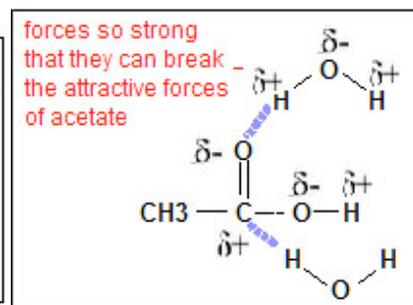
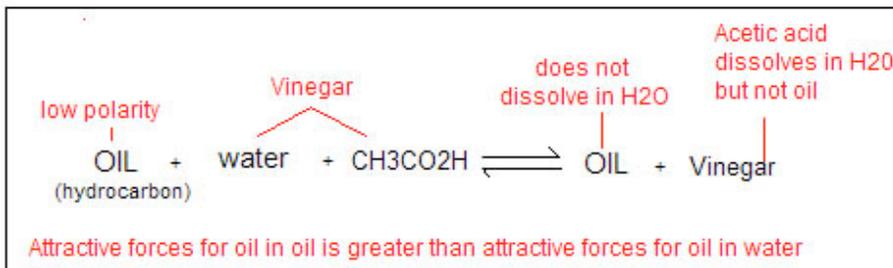
Like dissolves like. Polar molecules dissolve in polar solvents. Nonpolar molecules dissolve in nonpolar solvents.





- Even though the ionic forces in NaCl are very strong, the **MANY** water molecules that are attracted to each of the ions eventually break those bonds and create more numerous attractions. The great number of weak forces will add up and result in more stability for the atoms since the sum of all the forces gained will be greater than the few ionic forces. (quantity more important than quality of attraction)

Italian Dressing: (example from lecture)



Water - offers a lot of dipole, dipole interactions and a lot of opportunities for H-bonding

Oil - has nothing to offer to water except weak Van der Waals forces

- Because the solute-solvent bonds do not result in a more stable mixture, they do not dissolve each other together
- When the two liquids separate, the oil floats on top since it is less dense than vinegar and water