Get Your Forces Right!

First, what is a covalent bond?

**Covalent Bond**

**Definition:** The sharing of a pair of electrons through orbital overlap.

**Some examples:**

Methane, CH₄

![Methane molecular structure]

Cyclohexane, C₆H₁₂

![Cyclohexane molecular structure]

Covalent bonds are the **STRONGEST** chemical bonds!

Now, let's look at what exactly *noncovalent molecular forces* are…

**Noncovalent Molecular Forces**

**Definition:** The forces that exist between atoms or molecules. The forces may be attractive or repulsive. All noncovalent molecular forces are also known generally as van der Waals forces.

What is the fundamental basis behind noncovalent molecular forces?

*Electrostatic attractions!*
Now let’s take a closer look at how these noncovalent forces are distributed and classified:

**Decreasing Strength:** Cation-Anion, Dipole Interactions, London Forces

Physical properties that characterize noncovalent molecular forces?

As you go through the different forces, you will see how they are different (and similar) due to some of these different physical properties:

1. **Boiling point:** when the vapor pressure of a liquid is equal to the pressure surrounding the liquid.
   - What does that mean…?
     - Temperature at which the liquid enters the gaseous state – when surface liquid molecules are dislodged due to the breaking of bonds.
     - The energy to break these bonds is known as the heat of vaporization.
     - Higher heat of vaporization = higher boiling point!

   **Key point to keep in mind:** STRONGER bonds, attractions, and/or forces in a molecule = HIGHER boiling point for that molecule.

2. **Melting point:** the temperature at which a solid substance becomes a liquid.
   - When molecules of a solid acquire enough energy to break some bonds and gain movement.
   - The energy to break these bonds is known as the heat of fusion.
   - Higher heat of fusion = higher melting point!

   **Key point to keep in mind:** Melting point is not a very good measure of attractive forces. But the general trend: stronger bonds and forces = higher melting point.
How to use electronegativity to determine the time of bond:

Cation-Anion Forces (Ionic bonds)
Definition: a noncovalent molecular force that occurs between an anion and a cation due to electrostatic attractions (between the positive and negative charge.)

Some examples:

NaCl

ΔEN = 3.0 (Cl) – 0.9 (Na) = 2.1.

- Cl is much more EN than Na.
- Na easily loses its one electron to Cl so Cl can complete its octet.
- Leads to formation of positive cation, Na+, and negative anion Cl- to form ionic bond in NaCl.

MgO

ΔEN = 3.5 (O) – 1.2 (Mg) = 2.3.

Similar concept!
- Oxygen is far more EN than Mg
- Mg loses its electrons to oxygen forming an ionic bond.

NOTE!
The greater the charge, the greater the attraction between the anion and cation.

Physical characteristics and/or Significance:
High boiling point and melting point!

- Both evaporation and melting require the **separating** of these two ionic charges.
- Due to the extremely strong ionic bond between Na\(^+\) and Cl\(^-\), a **very high** amount of energy is required to **break** this bond.

**BOILING .....**
- High amount of energy needed to dislodge the surface NaCl molecules into separate Na\(^+\) and Cl\(^-\) ions.
- Heat of vaporization = 188 kcal/mol.
- Requires extremely high boiling point. Around 1,413° C!

**MELTING ....**
- Requires a **lot** of energy to break the strong bonds.
- The melting point of NaCl is around 801° C!

**Dipole Interactions**

1. **Ion-Dipole & Ion-Induced Dipole**
   
   **Definition:**
   - Ion Dipole: When one pole of a dipole is attracted to an oppositely charged ion. The negative pole of a dipole will be attracted to a cation (positive charge) and the positive pole of a dipole will be attracted to an anion (negative charge.)
   
   ![Anion Dipole Diagram](image)

   - Ion-Induced Dipole: When an ion approaches a molecule without a dipole and causes a change in the distribution of charges to induce a dipole.
     - For ex: an anion approaches a nonpolar molecule to create a dipole and gain attraction to the positive pole of the induced dipole.
A positively-charged cation inducing a dipole on molecule without a dipole

Example:
Ion Dipole: NaCl dissolved in water:
- Na\(^+\) is attracted to the \(\delta^-\) oxygen of water
- Cl\(^-\) is attracted to the \(\delta^+\) hydrogens of water

Physical characteristics and/or Significance:

Boiling and melting point relative to other noncovalent forces:

Dipole-Dipole Interactions < Ion-Dipole < Ionic Bonds

2. **Hydrogen Bonding**

**Definition:** An electrostatic interaction between the hydrogen and a lone pair of an atom.
- Hydrogen bond donor must have \(\delta^+\) charge that is large enough. This charge is comes from bonding to a highly electronegative element.
- The hydrogen bond acceptor must have a lone pair and high enough electron density.
  - H-bond acceptor must have a negative charge, unless it is oxygen or nitrogen.
- **NOTE:** Hydrogen bonding is not always a dipole-dipole interaction!
Some examples:

Physical characteristics and/or Significance:
- Compounds containing hydrogen bonds tend to have a high melting point, boiling point, and solubility.
  - Ex: proteins, alcohols, amines, DNA!

3. Dipole-Dipole
   Definition: When bond dipoles are attracted to opposite charges: the positive end of one dipole is attracted to the negative end of a second dipole (due to electrostatic attractions).

Some examples:
Physical characteristics and/or Significance:
Boiling and melting point relative to other noncovalent forces:

London Forces < Dipole-Dipole Interactions < Ion-Dipole < Cation-anion

4. **Cation-Pi**
   **Definition:** When a cation is electrostatically attracted to a pi electron cloud… (who would have guessed!)

![Diagram of Cation-Pi Interaction](image)

Example:
Physical characteristics and/or Significance:

- Protein structure: i.e. interaction of amine side chain with aromatic molecules
- Enzyme-substrate interactions
- Molecular binding and signaling
  - Ex: A ligand-gated channel, nicotinic acetylcholine receptor (nAChR) interacts with its neurotransmitter, acetylcholine, through cation-pi interactions.

The tryptophan is part of the nAChR with which acetylcholine interacts.

5. Pi stacking
   Definition: a noncovalent interaction that occurs between aromatic rings (also known as aromatic stacking.)

Example and Significance:

Remember back in the aromaticity unit, when we learned how the planarity of aromatic structures provide for stability and space conservation due to pi stacking… yeah. Here it is again! WOOOO!
AND LASTLY WE HAVE…

**London Forces:**

**Definition:** a noncovalent molecular force that results from the attraction between induced polarized electron clouds. It is found in all molecules in some way or another. The **WEAKEST** chemical interactions!

Electron cloud is not polarized when distance between atoms/molecules is too far.

As the molecules/atoms come closer, the electron clouds repel each other, become distorted, resulting in an induced polarized electron cloud.

**Examples:**
Characteristics to determine strength of LF’s:
There are many factors that influence the strength of these weak London Forces:

1. **Polarizability**: How easily you can distort an electron cloud
   - Atomic radius affects the polarizability. How? As the atomic radius increases, electrons move further away from the nucleus and are less affected by the pull of the nucleus. These electrons are less bound and can be easily moved and shifted around, and therefore more easily polarized.
   - Boiling Point: As the boiling point decreases, the attraction between the atoms and/or molecules also decreases. With weaker forces acting, the electron cloud will be more easily polarized.

2. **Surface Area**: some molecules may have the same polarizability, but different surface areas… what happens then?
   - The greater the surface area, the more space there is for the electrons of one molecule to come in proximity with its neighboring molecule.
   - Although the polarizability is the same, there is more area to be polarized. This allows for a greater attraction.
   - LARGER surface area = HIGHER boiling point = GREATER London force!
So, London forces also increase with **molecular weight**? No…

- The molecular weight may be the same, but as surface area increases, the force and the boiling point increase!
- It’s NOT the molecular weight!
- Let’s look at the example Dr. H went over in class one more time…
  - $C_5H_{12}$

**DECREASING SURFACE AREA**
**DECREASING BOILING POINT**
**DECREASING LONDON FORCES**

Let’s END by recapping the relative strengths of all the **Noncovalent Forces:**

<table>
<thead>
<tr>
<th><strong>WEAKEST</strong> Force:</th>
<th><strong>STRONGEST</strong> Forces:</th>
</tr>
</thead>
<tbody>
<tr>
<td>London Forces</td>
<td>Covalent bonds (the strongest)</td>
</tr>
<tr>
<td></td>
<td>Cation-anion (Ionic bonds)</td>
</tr>
</tbody>
</table>

(Does not mean all are of equal strength)
INCREASING STRENGTH

I hope this tutorial was helpful in understanding the different noncovalent molecular forces and their unique characteristics and functions!

Good luck with everything! 😊

SOURCES

Dr.Harding’s Thinkbook
Dr.Harding’s Lecture Supplement

Wikipedia for information and images:
http://en.wikipedia.org/wiki/Boiling_point
http://en.wikipedia.org/wiki/Magnesium
http://en.wikipedia.org/wiki/DNA
http://en.wikipedia.org/wiki/Cyclohexane_conformation
http://en.wikipedia.org/wiki/Cation%E2%80%93pi_interaction
http://upload.wikimedia.org/wikipedia/commons/thumb/e/e1/Benzene-sodium.png/150px-Benzene-sodium.png
http://en.wikipedia.org/wiki/File:NaCl.png

Miscellaneous sources for information and images:
http://www.chemprofessor.com/imf_files/image015.jpg
i.ucdavis.edu/@api/deki/files/13855/=POLA.jpg
http://www.science.uwaterloo.ca/~cchieh/cact/c123/intermol.html
http://classes.kvcc.edu/chm220/Images/c5h12.jpg
http://proteopedia.org/wiki/images/d/d2/Cation-pi-dougherty.jpg
http://www.chem.ufl.edu/~itl/2041_f97/matter/FG11_005.GIF
http://i01.i.aliimg.com/photo/v0/105064697/REFINED_SALT_SODIUM_CHLORIDE_NALC_99_25.jpg
http://www.school-for-champions.com/chemistry/images/bonding_types-nacl.gif