

The Four Intermolecular Forces and How They Affect Boiling Points

It's amazing how much chemistry comes down to simple attraction between opposite charges and repulsion between like charges.

This is the driving force behind [chemical bonding](#), of course. But it's also responsible for the forces *between* molecules. This means that *properties like melting and boiling points are a measure of how strong the attractive forces are between individual atoms or molecules.*

There are four types of these interactions and they are all different manifestations of “opposite charges attract”.

It all flows from this general principle: as bonds become more polarized, the charges on the atoms become greater, which leads to greater intermolecular attractions, which leads to higher boiling points.

Ionic bonds > H bonding > Van der Waals dipole-dipole interactions > Van der Waals dispersion forces.

1. Ionic forces are interactions between charged atoms or molecules. Positively charged ions, such as $\text{Na}(+)$, $\text{Li}(+)$, and $\text{Ca}(2+)$, are termed [cations](#). Negatively charged ions, such as $\text{Cl}(-)$, $\text{Br}(-)$, $\text{HO}(-)$ are called anions (I always got this straight through remembering that the “N” in “Anion” stood for “Negative”) The attractive forces between oppositely charged ions is described by [Coulomb's Law](#), in which the force increases with charge and as decreases as the distance between these ions is increased. The highly polarized (charged) nature of ionic molecules is reflected in their high melting points (NaCl has a melting point of $801\text{ }^{\circ}\text{C}$) as well as in their high water solubility (for the alkali metal salts, anyway; metals that form [multiple charges](#) like to leave residues on your bathtub)

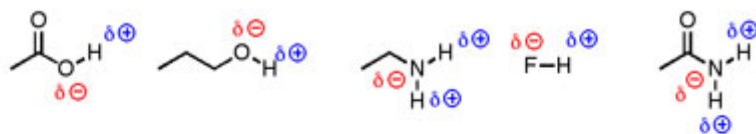
1. Ionic forces - attraction between point charges



- **cations** - positively charged (e.g. Na^+ , K^+ , Li^+ , NH_4^+)
- **anions** - negatively charged (e.g. Cl^- , I^- , F^-)

2. Hydrogen bonding occurs in molecules containing the highly electronegative elements F, O, or N directly bound to hydrogen. Since H has an electronegativity of 2.2 (compare to 0.9 for Na and 0.8 for K) these bonds are not as polarized as purely ionic bonds and possess some covalent character. However, the bond to hydrogen will still be polarized and possess a dipole.

2. Hydrogen bonding



Electronegativity of F = 4.0
Electronegativity of O = 3.4
Electronegativity of N = 3.0

Electronegativity of H = 2.0

H-bonding in action: transient attractions between dipoles



- Strength increases with electronegativity
- H-bonding increases boiling points

DRAMATICALLY!

CH₄ → b.p. of -161°C
mol. weight = 16
H₂O → b.p. of 100°C
mol. weight = 18

The dipole of one molecule can align with the dipole from another molecule, leading to an attractive interaction that we call [hydrogen bonding](#). Owing to rapid molecular motion in solution, these bonds are transient (short-lived) but have significant bond strengths ranging from (9 kJ/mol (2 kcal/mol) (for NH) to about 30 kJ/mol (7 kcal) and higher for HF. As you might expect, the strength of the bond increases as the electronegativity of the group bound to hydrogen is increased.

So in a sense, HO, and NH are “sticky” - molecules containing these functional groups will tend to have higher boiling points than you would expect based on their molecular weight.

3. Van Der Waals Dipole-dipole interactions.

Other groups beside hydrogen can be involved in polar covalent bonding with strongly electronegative atoms. For instance, each of these molecules contains a dipole:

3. Dipole-dipole interactions

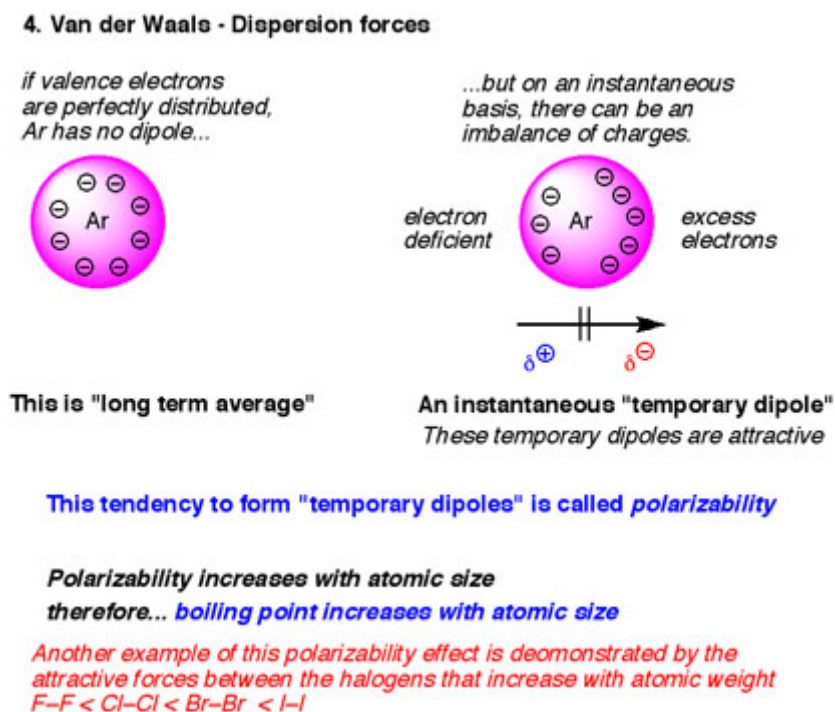


- Dipoles created by differences in electronegativities
- Interaction between dipoles is attractive
- Similar to H-bonding, but C is more electronegative (2.5) than H (2.2).
Therefore - magnitude of dipoles are smaller

These dipoles can interact with each other in an attractive fashion, which will also increase the boiling point. However since the electronegativity difference between carbon (electronegativity = 2.5) and the electronegative atom (such as oxygen or nitrogen) is not as large as it is for hydrogen (electronegativity = 2.2), the polar interaction is not as strong. So on average these forces tend to be weaker than in hydrogen bonding.

4. Van der Waals Dispersion forces (London forces)

The weakest intermolecular forces of all are called [dispersion forces](#) or London forces. These represent the attraction between *instantaneous dipoles* in a molecule. Think about an atom like argon. It's an inert gas, right? But if you cool it to $-186\text{ }^{\circ}\text{C}$, you can actually condense it into liquid argon. The fact that it forms a liquid it means that *something* is holding it together. That "something" is dispersion forces. Think about the electrons in the valence shell. *On average*, they're evenly dispersed. But at any given instant, there might be a mismatch between how many electrons are on one side and how many are on the other, which can lead to an *instantaneous* difference in charge.



It's a little like basketball. *On average*, every player is covered one-on-one, for an even distribution of players. But at any given moment, you might have a double-team situation where the distribution of players is "lumpy" (it also means that somebody is open). In the valence shell, this "lumpiness" creates dipoles, and it's these dipoles which are responsible for intermolecular attraction.

The *polarizability* is the term we use to describe how readily atoms can form these instantaneous dipoles. ***Polarizability increases with atomic size.*** That's why the boiling point of argon ($-186\text{ }^{\circ}\text{C}$) is so much higher than the boiling point of helium ($-272\text{ }^{\circ}\text{C}$). By the same analogy, the boiling point of iodine, (I-I, $184\text{ }^{\circ}\text{C}$) is much higher than the boiling point of fluorine (F-F, $-188\text{ }^{\circ}\text{C}$).

For hydrocarbons and other non-polar molecules which lack strong dipoles, these dispersion forces are really the only attractive forces between molecules. Since the dipoles are weak and transient, they depend on contact between molecules – which means that the forces increase with surface area. A small molecule like methane has very weak intermolecular forces, and has a low boiling point. However, as molecular weight increases, boiling point also goes up. That's because the surface over which these forces can operate has increased. Therefore, **dispersion forces increase with increasing molecular weight.** Individually, each interaction isn't worth much, but if collectively, these forces can be extremely significant. How can a gecko lizard walk on walls? Look at its [feet](#).

Dispersion forces are a "surface area" phenomenon

•Hydrocarbons bind together through dispersion forces

•Alkane boiling points increase with chain length. This is due to their increased surface area available for dispersion forces.

Boiling point increases with molecular weight

Methane	Ethane	Propane	Butane	Pentane	Hexane	Heptane	Octane
-164 °C	-89 °C	-42 °C	-0.5 °C	36 °C	69 °C	98 °C	125 °C

[Determining trends for hydrocarbons can get a little bit tricky depending on the exact structure - symmetry also plays a role in boiling points and melting points. I talked about this in detail [previously](#).]

Bottom line:

1. The intermolecular forces increase with increasing polarization of bonds.
2. Strength of forces (and therefore impact on boiling points) is ionic > hydrogen bonding > dipole dipole > dispersion
3. Boiling point increases with molecular weight, and with surface area.