

3 Trends That Affect Boiling Points

Figuring out the order of boiling points is all about **understanding trends**. The key thing to consider here is that boiling points reflect the strength of forces between molecules. The more they stick together, the more energy it will take to blast them into the atmosphere as gases.

There are 3 important trends to consider.

1. The relative strength of the four intermolecular forces is:

Ionic > Hydrogen bonding > dipole dipole > Van der Waals dispersion forces.

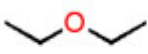
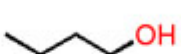

The influence of each of these attractive forces will depend on the functional groups present.

2. Boiling points increase as the number of carbons is increased.
3. Branching decreases boiling point.

Trend #1: The relative strength of the four intermolecular forces .

Compare the different butane alcohol derivatives shown below. Molecules of diethyl ether, $C_4H_{10}O$, are held together by dipole-dipole interactions which arise due to the polarized C-O bonds. Compare its boiling point of (35 °C) with that of its isomer butanol (117 °C). The greatly increased boiling point is due to the fact that butanol contains a hydroxyl group, which is capable of hydrogen bonding. Still, the attractive forces in butanol pale in comparison to those of the salt sodium butoxide, which *melts* at an extremely high temperature (well above 260 °C) and actually decomposes before it can turn into a liquid.

Boiling Points Reflect Intermolecular Attractive Forces Example - Alcohol derivatives (of similar molecular weight)



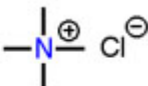
			
Mol. weight	74.12	74.12	96.1
Name	Diethyl ether	<i>n</i> -butanol	Sodium <i>n</i> -butoxide
Strongest intermolecular force	DIPOLE-DIPOLE	HYDROGEN BONDING	IONIC
Boiling point	35 °C	117 °C	> 260 °C

Then think about butane, C_4H_{10} , which contains no polar functional groups. The only attractive forces between individual butane molecules are the relatively weak Van der Waals dispersion forces. The result is that butane boils at the temperature at which water freezes (0° C), far below even that of diethyl ether.

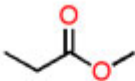
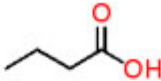
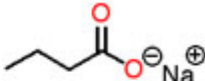
Moral of the story: among molecules *with roughly similar molecular weights*, the boiling points will be determined by the functional groups present.

You could tell a similar tale for the similar amine and carboxylic acid isomers shown below.

Amine derivatives (of similar molecular weight)

			
Mol. weight	73.1	73.1	109.6
Name	<i>N,N</i> -dimethyl ethylamine	<i>n</i> -butylamine	Tetramethyl ammonium chloride
Strongest intermolecular force	DIPOLE-DIPOLE	HYDROGEN BONDING	IONIC
Boiling point	36 °C	77 °C	> 260 °C

Carboxylic acid derivatives (roughly similar molecular weight)










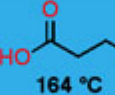
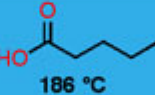
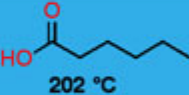



			
Mol. weight	88.1	88.1	111.1
Name	Methyl propionate	Butyric acid	Sodium butanoate
Strongest intermolecular force	DIPOLE-DIPOLE	HYDROGEN BONDING	IONIC
Boiling point	80 °C	163 °C	> 260 °C

BOTTOM LINE: Intermolecular forces go in the order
ionic > **Hydrogen bonding** > **Dipole-dipole** > Van der Waals
 dispersion forces (London forces).

Trend #2 – For molecules with a given functional group, boiling point increases with molecular weight.

Look at the dramatic increases in boiling points as you increase molecular weight in all of these series:

In a given series, boiling point increases with molecular weight. **Why?**

ALKANES				
Boiling point	-42 °C	0 °C	36 °C	69 °C
ALCOHOLS				
Boiling point	97 °C	117 °C	138 °C	158 °C
CARBOXYLIC ACIDS				
Boiling point	141 °C	164 °C	186 °C	202 °C
ETHERS				
Boiling point	-24 °C	35 °C	89 °C	

Increasing surface area gives rise to increased Van Der Waals interactions

Here's the question: **How**, exactly do intermolecular forces increase as molecular weight increases?

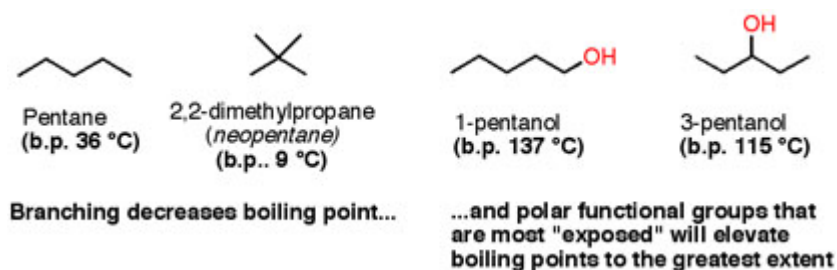
Well, the key force that is acting here are [Van der Waals dispersion forces](#), which are **proportional to surface area**. So as you increase the length of the chain, you also increase the surface area, which means that you increase the ability of individual molecules to attract each other.

On an intuitive level, you could compare these long molecules to strands of spaghetti - the longer the noodles, the more work it takes to pull them apart. As the chain length increases, there will be regions where they can line up next to each other extremely well.

Individually, each interaction might not be worth very much, but when you add them all up over the length of a chain, Van der Waals dispersion forces can exert tremendous effects.

3. Symmetry (or lack thereof).

This is another byproduct of the surface-area dependence of Van der Waals dispersion forces – the more rod-like the molecules are, the better able they will be to line up and bond. To take another intuitive pasta example, what sticks together more: spaghetti or macaroni? The more spherelike the molecule, the lower its surface area will be and the fewer intermolecular Van der Waals interactions will operate. Compare the boiling points of pentane (36°C) and 2,2-dimethyl propane (9 °C).



It can also apply to hydrogen bonding molecules like alcohols – compare the boiling points of 1-pentanol to 2-pentanol and 3-pentanol, for instance. The hydroxyl group of 1-pentanol is more “exposed” than it is in 3-pentanol (which is flanked by two bulky alkyl groups), so it will be better able to hydrogen bond with its fellows.

In summary, there are three main factors you need to think about when confronted with a question about boiling points. 1) what intermolecular forces will be present in the molecules? 2) how do the molecular weights compare? 3) how do the symmetries compare?

One last quick question for the road:

Which of these three amine isomers will have the highest boiling point, and why?

