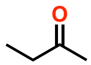
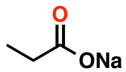
What To Expect When Being Asked Boiling Point Questions On Exams

First thing to know: you'll be expected to understand **trends** in boiling points - **not** absolutes.

E.g. "which of these molecules will have the highest/lowest boiling point", or "rank these molecules in order of increasing/decreasing boiling point".
NOT - "give the boiling point of this molecule".


A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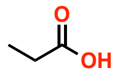
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D

Determining the exact boiling point of a molecule can only be done experimentally - **by measurement.**
Guessing *trends*, however - which molecule in a given set will have the highest or lowest boiling point - is very doable.
Here are three key trends that will help to answer >90% of typical boiling point questions. More details are provided on the following pages.

Trend #1: Forces

stronger forces = higher boiling point
(all else being equal)

With molecular weight roughly constant, **boiling point increases according to the types of intermolecular forces present in the molecule.**

There are 4 general "types" of intermolecular forces, which are determined by the functional groups present

- **ionic forces** (salts)
- **hydrogen bonding** (alcohols, carboxylic acids, amines)
- **dipole-dipole forces** (carbon bound to electronegative groups like O, N, Cl, etc.)
- **London (dispersion) forces** - present in all molecules, but most prominent for hydrocarbons, since they lack the previous three

KEY TREND: **ionic forces** are stronger than **hydrogen bonding** which is stronger than **dipole-dipole** forces, which are stronger than **London (disperson)** forces

More details on these in the next page.

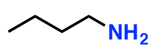
Trend #2: Size

increasing # of carbons = increasing boiling point
(among molecules with identical functional groups)

With the *types* of forces constant, boiling point will increase with an increasing number of carbons

Boiling point incresaes with increased surface area, which increases as the carbon chain is lenghtened.

Examples of the trend:


butylamine
351 K
(78 °C)

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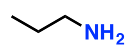
propylamine
322 K
(49 °C)

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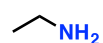
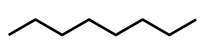

ethylamine
291 K
(18 °C)


C_8H_{18}
398 K
(125 °C)

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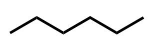
C_6H_{14}
341 K
(68 °C)

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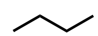
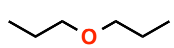

C_4H_{10}
272 K
(–1 °C)


dipropyl ether
363 K
(90 °C)

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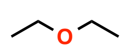
diethyl ether
307 K
(34 °C)

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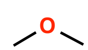
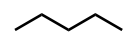

dimethyl ether
249 K
(–24 °C)

Note that these all share the same functional groups. The only variable changing here is the size of the carbon chain.

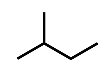
Trend #3: Surface Area

increasing surface area = increasing boiling point
(among molecules with identical functional groups that have the same # of carbons)

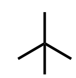
With the types of forces constant and molecular weight constant, boiling point increases wtih increased surface area


C_5H_{12}
310 K
(36 °C)
linear
(Highest surface area)

>


C_5H_{12}
300 K
(27 °C)
branched

>


C_5H_{12}
283 K
(10 °C)
highly branched
(Most sphere-like: lowest surface area)

For more information, check the next page

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What Is Boiling, Anyway?

- Technically, "boiling" occurs when the **vapor pressure** of a liquid is equal to the **atmospheric pressure**.
- The **boiling point** (bp) of a substance is the temperature at which this occurs.
- Lowering the atmospheric pressure will lower the boiling point

The separation between molecules is **much greater in a gas than a liquid**

In order for boiling to occur, there must be sufficient energy present to separate molecules from the intermolecular forces that hold them together.

- Boiling point essentially measures the energy required to overcome the intermolecular forces in a liquid

The stronger the intermolecular forces, the higher the boiling point

Strong intermolecular forces --> more energy required to convert liquid to gas ---> higher boiling point

Water is a good example: **H_2O b.p. 100°C (373 K)**

Weak intermolecular forces --> less energy required to convert liquid to gas ---> lower boiling point

A good example is the noble gas Argon **Argon b.p. –185 °C (87 K)**

Volatility is a *qualitative* measure of boiling point. A liquid with low boiling point is said to be highly **volatile**

What Makes Molecules "Stick" Together?

In other words, what determines the strength of attraction between molecules?

In a nutshell: Electrostatic forces - attraction between opposite charges

What determines how large that force is?

Ultimately this is determined by the Coulomb equation

Coulomb's constant

$$F = k_e \frac{q_1 q_2}{r^2}$$

magnitude of charge #1

magnitude of charge #2

distance between charges

magnitude of force

For boiling point, the key lesson is:

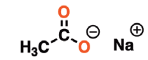
the larger the charges, the greater the attractive force

and

the greater the attractive forces between molecules, the greater the boiling point

What Determines The Size of The Charges?

Compounds with **ionic bonding** have high boiling (and melting) points because of the attractve forces between point charges.



Attraction is strong because we're dealing with full point charges, not partial charges

Most molecules have some degree of **polar covalent** bonding, where there is a **dipole** - a difference in **electronegativity** between atoms that leads to partial charges.

Example: HCl

δ^+ δ^-
H–Cl

Electronegativity

Hydrogen: 2.2
Chlorine : 3.2

Since chlorine is more electronegative, it draws the shared pair of bonding electrons towards itself, resulting in a greater negative charge (represented as δ^-)

Another Example: CH_3OH

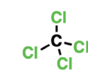
δ^+ δ^- δ^+
H_3C–O–H

Electronegativity

Hydrogen: 2.2
Oxygen: 3.4
Carbon: 2.5

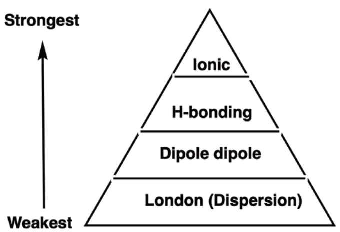
The O-H dipole is greater than the O-C dipole due to greater electronegativity difference

Dipoles are vectors. Be aware that in some cases, the vector sum of the dipoles can be zero, e.g. with CCl_4



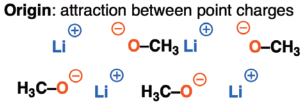
No dipole moment in tetrahedral CCl_4

The Four Intermolecular Forces, From Strongest To Weakest



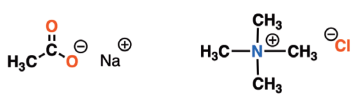
Ionic Forces (Strongest)

Origin: attraction between point charges



How to recognize:

- Do you see any point charges drawn (i.e. ⊕ ⊖) That's a telltale sign of ionic bonding.



- Do you see any electropositive metals (e.g. Na, K, Li, Mg) that are bound to a very electronegative atom such as O or N?

CH_3ONa ***t*-BuOLi** **KOEt**

Charges are often not drawn in, but they still exist!

These are also ionic compounds and will have high boiling points
(in practice they generally decompose before boiling, but for the sake of answering exam questions, they have the highest bp's)

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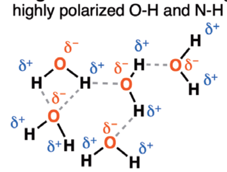
Hydrogen bonding

Origin: attraction between large partial charges in highly polarized O-H and N-H bonds



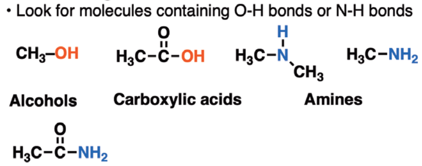
Electronegativity of O 3.4

Electronegativity of N 3.0

Electronegativity of H 2.2

How to recognize:

- Look for molecules containing O-H bonds or N-H bonds



Different Strengths Of Hydrogen Bonding
Hydrogen bonding with O–H is stronger than hydrogen bonding with N–H

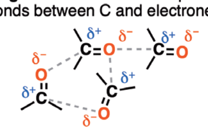
e.g. H_2O boiling point 100°C NH_3 boiling point –33 °C

This is because of the greater electronegativity difference between O-H compared to N-H

For more great "cheat sheets", visit the MOC Study Guide Homepage

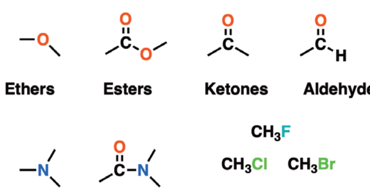
Dipole-dipole forces

Origin: attraction between partial charges in bonds between C and electronegative atoms



How to recognize:

- Look for bonds between **carbon** and electronegative atoms like **O, N, and halogens (F, Cl, Br, I)**

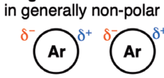


This is weaker than hydrogen bonding because the electronegativity difference between carbon and oxygen / nitrogen / halogens is not as large

Since the partial charges are smaller, the intermolecular forces are weaker, and the effect on boiling point is smaller.

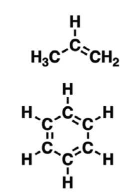
London Dispersion Forces (Weakest)

Origin: attraction between instantaneous dipoles in generally non-polar atoms or molecules



These instantaneous dipoles arise from temporary fluctuations in electron density in the atom. Present in **all atoms.**

How to recognize: present in all molecules, but is the *only* significant intramolecular force in hydrocarbons, since their permanent dipoles are generally very weak



$CH_3CH_2CH_2CH_3$

$H_3C–C{\equiv}C–CH_3$

Key Point: Increases with surface area

The strength of these interactions between molecules **increases as a function of their surface area**.

Think of them like very small suction-cups. Each individual point of contact is weak, but dozens of them can add up to a strong intermolecular force.

CH_4	CH_3CH_3	$CH_3CH_2CH_3$
111 K	184 K	398 K

In practice this generally means **boiling point increases with increasing molecular weight**

Page 3 : Specific Problem Solving Advice

Problem type #1 : Ranking according to type of force

General procedure

Try to categorize molecules by the strongest force you see present in them, and then rank by the criteria ionic > hydrogen bonding > dipole-dipole > London forces.

For hydrogen bonding: multiple H-bonding functional groups will lead to a higher overall boiling point (see below).

Question #1: Rank the following molecules in order of boiling point:

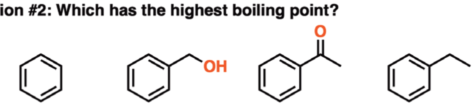
$CH_3CH_2CH_2CH_3$	$CH_3CH_2OCH_3$	$CH_3CHOHCH_2CH_3$	$(CH_3)_3C\text{-}ONa$
A	B	C	D

Following the procedure, we see that D contains an ionic bond (so will have highest boiling point). C contains a hydrogen bond (next highest - see that OH?). B contains dipole-dipole interactions (next highest). A has no significant dipoles and has only London dispersion forces.

We can therefore rank the boiling points according to the categories that their functional groups belong to.

D > C > B > A

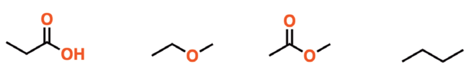
Question #2: Which has the highest boiling point?



A B C D

We look for the strongest force present in each molecule. In A) we see only London forces, in B we see hydrogen bonding, in C we see dipole-dipole, and D only London forces. Since B has the strongest force present, it will have highest BP.

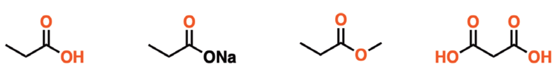
Question #3: Which has the highest boiling point?



A B C D

Again looking for the strongest forces present, we see hydrogen bonding in A), dipole-dipole in B), dipole-dipole in C), and London forces in D. Since hydrogen bonding is the strongest force present here, the answer is A.

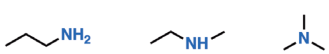
Question #4: Rank these molecules in order of boiling point (highest to lowest)



A B C D

Looking for the strongest forces present, we see hydrogen bonding in A), ionic in B), dipole-dipole in C), and hydrogen bonding in D. Ionic is strongest (B) and dipole-dipole is weakest (C). How to tell between A and D ? Note that D) has twice as many hydrogen bond donors. There will be more hydrogen bonding, therefore it will have a higher boiling point. Order is B > D > A > C

Question #5: Which has the highest boiling point?



A B C

Molecules A and B have hydrogen bonding, whereas C only has dipole-dipole (no N-H bonds!). How do we determine whether A or B will have a higher boiling point? Notice that A) has two N-H bonds whereas B) only has one. Therefore A) should have twice as much hydrogen bonding and therefore a higher boiling point. A > B > C

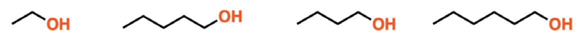
Problem type #2 : Ranking according to molecular weight

If you notice that the molecules all have similarly strong forces, then the next thing to do is to try to categorize them by molecular weight.

Increasing molecular weight is correlated with increasing London dispersion forces, which will lead to higher boiling points.

They should all have similar functional groups

Question #1: Rank the following molecules in order of boiling point:



A B C D

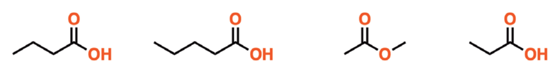
Here we see that all the molecules have OH groups, and thus hydrogen bonding is the strongest force present. Their boiling points will increase in order of their molecular weight. D (hexanol, 430 K) > B (pentanol, 411 K) > C (butanol, 391 K), A (ethanol, 351 K)

Question #2: Rank the following molecules in order of boiling point:

A B C D

All of these molecules are hydrocarbons, and have no stronger force than London (dispersion) forces. Their boiling points will increase with increasing molecular weight. D (heptane, 372 K) > A (hexane, 341 K) > C (pentane, 309 K) > B (butane, 272 K)

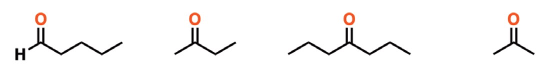
Question #3: Rank these molecules in order of boiling point



A B C D

All of these molecules except for C are carboxylic acids. Normally it's difficult to predict what will happen when the trends are mixed, but here, C has a comparable molecular weight to D, the smallest carboxylic acid. It's safe to say that C will have a lower boiling point than D. So the order should go B (pentanoic acid, largest) > A (butanoic acid) > D (propanoic acid) > C (methyl ethanoate)

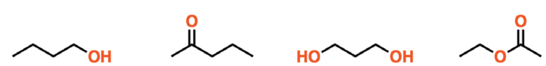
Question #4: Rank these molecules in order of boiling point



A B C D

All of these molecules have dipole-dipole forces (it's important to note that A does NOT have hydrogen bonding - it's an aldehyde. They can be ranked by molecular weight. C has the most carbons (7) so the ranking should go C > A > B > D

Be prepared to answer questions like this if they're written in condensed formula, e.g. A written as C_4H_9CHO or C written as $CH_3(CH_2)_2C(O)CH_2CH_2CH_3$



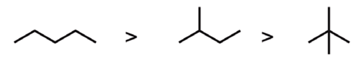
A B C D

Looking for the strongest forces present, we see hydrogen bonding (A), dipole-dipole (B), hydrogen bonding (C) and dipole-dipole (D). How to pick between A) and C) ? C has twice as many alcohol groups, so it should have stronger intermolecular forces and therefore a higher boiling point.

Problem type #3: Branching

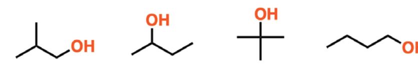
If they all have similar functional groups AND have similar molecular weights, then try to differentiate them by branching.
More branching = more sphere-like. Remember that a sphere has the lowest surface area/volume ratio, and since boiling point is surface area dependent, all else being equal spherical molecules will have lower boiling points.

The classic example:



C_5H_{12}	C_5H_{12}	C_5H_{12}
310 K (36 °C)	300 K (27 °C)	283 K (10 °C)
linear	**branched**	**highly branched**

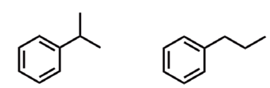
Question #1: Which has lowest boiling point?



A B C D

All these alcohols have the same molecular weight. C) is the most branched (has the shortest carbon chain). It should have the lowest bp (and it does: 355 K). D) has the highest bp (391 K). B) and A) are harder to predict relative to each other.

Question #2: Which of these isomers of propylbenzene will have the highest boiling point?

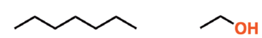


A B

Molecule B has the longest carbon chain (least branching) and should have the highest boiling point.
Actual values: B = 432 K, A = 425 K.

What about questions like this:

Which will have the highest boiling point?



A B

It's too hard to predict the answer to this question. Why? Because the trends operate in opposite directions. B) has the strongest force (hydrogen bonding) but A) has a much higher molecular weight.
The point of these exercises is to get you in the habit of spotting trends! When the trends are mixed and set in opposite directions like this, it defeats the purpose of the exercise.

questions, comments, corrections:
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