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".

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.

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**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 (dispersion) 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 increases with increased surface area, which increases as the carbon chain is lengthened.

Examples of the trend:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>butylamine</td>
<td>351 K (78 °C)</td>
</tr>
<tr>
<td>propylamine</td>
<td>322 K (49 °C)</td>
</tr>
<tr>
<td>ethylamine</td>
<td>291 K (35 °C)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₄</td>
<td>341 K (68 °C)</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>398 K (125 °C)</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>272 K (−1 °C)</td>
</tr>
</tbody>
</table>

For more information, check the next page

**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 with increased surface area.

Examples of the trend:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>dipropyl ether</td>
<td>291 K (−1 °C)</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>307 K (34 °C)</td>
</tr>
<tr>
<td>dimethyl ether</td>
<td>249 K (−24 °C)</td>
</tr>
</tbody>
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Note that these all share the same functional groups. The only variable changing here is the size of the carbon chain.
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: H₂O 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.

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 Makes Molecules "Stick" Together?

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

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

- for boiling point, the key lesson is:

What Determines The Size of The Charges?

H₂C = O

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

H₂C - O = H

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

\[ \delta^- \quad \delta^- \]

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 $\delta^-$).

Another Example: CH₃OH

\[ \delta^- \quad \delta^- \quad \delta^- \]

H - C - O - H

Electronegativity

Hydrogen: 2.2
Oxygen: 3.4
Carbon: 2.5

Dipoles are vectors. Be aware that in some cases, the vector sum of the dipoles can be zero, e.g., with CO₂.

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Problem type #1: Ranking according to type of force

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:

\[
\begin{align*}
\text{C}_8\text{H}_{16} \quad & \quad \text{C}_8\text{H}_{16} \quad & \quad \text{C}_8\text{H}_{16} \quad & \quad \text{C}_8\text{H}_{16}
\end{align*}
\]

Following the procedure, we see that C contains a hydrogen bond (so will have highest boiling point), B contains a dipole-dipole bond (next highest), and A has no dipole-dipole bond and therefore will have the lowest boiling point.

They should all have similar functional groups.

Question #2: Which has the highest boiling point?

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) must be highest BP.

Question #3: Which has the highest boiling point?

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.

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:

\[
\begin{align*}
\text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH}
\end{align*}
\]

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, 301 K)

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

\[
\begin{align*}
\text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH}
\end{align*}
\]

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:

\[
\begin{align*}
\text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH}
\end{align*}
\]

All of these molecules except for C are carboxylic acids. Normally it's difficult to predict what will happen which factor is most important 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 acetate)

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:

\[
\begin{align*}
\text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH} \quad & \quad \text{C}_3\text{H}_7\text{OH}
\end{align*}
\]

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, 301 K)

Question #1: Which has the lowest boiling point?

All these alcohols have the same molecular weight. C is the 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?

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?

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.

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

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