

# Intermolecular Forces

## Properties of Liquids

Stronger intermolecular forces → molecules are more attracted to each other → they stick together better → they are harder to separate from each other.

Strong IMF's lead to high boiling points, low vapor pressures, and high heats of vaporization.

## Types of Forces

### London Dispersion Forces/ Induced Dipole-Induced Dipole forces

A temporary dipole on one molecule (formed by the random motion of electrons in the molecule) induces a temporary dipole on neighboring molecules. These temporary dipoles experience attraction for each other.

London forces exist between all types of molecules. The strength of London forces depends on the molar mass of the molecule (higher MM → more electrons → more polarizable → stronger London forces) and, to a lesser extent, on surface area (greater surface area → stronger London forces).

### Dipole-Dipole Forces

Polar molecules align themselves so that the  $\delta^-$  end of one molecule is near the  $\delta^+$  ends of other molecules. The molecules are thus attracted to each other.

Dipole-dipole forces exist between polar molecules. The greater the polarity, the stronger the dipole-dipole forces.

### Hydrogen Bonding

This is a special (stronger) case of dipole-dipole forces. It can exist between a molecule with a hydrogen atom directly attached to an N, O, or F atom and another molecule with a lone pair of electrons on an N, O, or F. The atoms N, O, and F are all very electronegative and very small. When a hydrogen atom is bonded to an N, O, or F, the resulting bond is especially polar. The  $\delta^+$  hydrogen atom is "shared" between two atoms of N, O, or F: the hydrogen atom has a covalent bond to one and a hydrogen bond to the other. Hydrogen bonds are very directional; the three atoms must lie in a straight line.

## Analysis

When you are asked to compare boiling points or vapor pressures for a set of molecules:

1. Find the approximate molar mass of each molecule.
2. Determine the types of intermolecular forces present for each molecule.

Any molecule has London forces. Polar molecules have dipole-dipole forces. Molecules with a hydrogen atom attached to N, O, or F can hydrogen bond.

- If the molecules have similar molar masses, their London forces have similar strengths. Look at the types of intermolecular forces each molecule has. The one with the most types of forces has the strongest IMF's overall.
- If the molecules have similar molar masses and they are all nonpolar, consider surface area. The more stretched-out one (least compact) has the higher surface area and thus will have stronger London forces. (And stronger IMF's overall, since London forces are the only types of forces they have.)
- If the molecules have similar molar masses and similar types of intermolecular forces, look for the one that is the most polar or that has the most electronegative atoms or the most hydrogen bonding groups. That one will have the strongest IMF's overall.
- If the molecules have very different molar masses (by a factor of 2 or more), then they have very different London force strengths. In this case, the one with the much higher molar mass will have the strongest intermolecular forces overall.

### Examples

- |                                     |                                  |                                   |
|-------------------------------------|----------------------------------|-----------------------------------|
| $\text{CH}_3\text{CH}_2\text{CH}_3$ | $\text{CH}_3\text{CH}_2\text{F}$ | $\text{CH}_3\text{CH}_2\text{OH}$ |
| MM 44, bp $-42^\circ\text{C}$       | MM 48, bp $-38^\circ\text{C}$    | MM 46, bp $78^\circ\text{C}$      |

These molecules have very similar molar masses, so their London forces are similar. However, the first one is nonpolar and has only London forces. The second one is polar because it contains F, but it cannot hydrogen bond because it does not have H attached directly to the F. The last one is polar and can hydrogen bond because of the OH group. The one that can H-bond has the highest bp, the polar one has the medium bp, and the nonpolar one has the lowest bp.

- |  |   |
|--|---|
| $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ | $\text{CH}_3$<br>$\text{CH}_3\text{CHCH}_3$ |
| MM 58, bp $-0.5^\circ\text{C}$                 | MM 58, bp $-12^\circ\text{C}$               |

These molecules are both nonpolar and have the same molar mass. However, the first one is more stretched out and the second one is more compact. The first one has a higher surface area and therefore stronger London forces and a higher boiling point. (Since they are nonpolar, the only IMF they have is London forces.)

- |                                   |                               |
|-----------------------------------|-------------------------------|
| $\text{CH}_3\text{CH}_2\text{OH}$ | $\text{CH}_3\text{OCH}_3$     |
| MM 46, bp $78^\circ\text{C}$      | MM 46, bp $-25^\circ\text{C}$ |

These molecules have the same molar mass. The first one can hydrogen bond, but the second one cannot (even though it is polar). Since the first one can hydrogen bond, it has stronger IMF's overall and a higher boiling point. (Note what a huge difference there is in the boiling points!)

4.       $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$                        $\text{CH}_3\text{CH}_2\text{OH}$   
          MM 100, bp  $98^\circ\text{C}$                       MM 46, bp  $78^\circ\text{C}$

These molecules have very different molar masses. The molar mass of the first one is more than 2 times the molar mass of the second one. Even though the second one can hydrogen bond and the first one is nonpolar, the first one has stronger IMF's overall. The one with the higher molar mass has much stronger London forces than the other one.

## Solubility

When deciding relative solubilities, the overall concept is "like dissolves like". Molar mass is no longer important. Instead, look at types of intermolecular forces.

Polar molecules are soluble in polar solvents.

Nonpolar molecules are soluble in nonpolar solvents.

Polar and nonpolar substances do not mix.

Many organic molecules contain a polar section and a nonpolar section. If the nonpolar section is long, the substance probably won't be soluble in polar solvents (like water). If the molecule is long and also has lots of hydrogen bonding groups, it probably will be soluble in water.

## Examples

1.  $\text{CH}_3\text{CH}_2\text{OH}$  is completely soluble in water. It can form hydrogen bonds with water, and its hydrocarbon section is small.
2.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  is insoluble in water. It can form hydrogen bonds, but its nonpolar section long, so it is mostly nonpolar.
3.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is completely insoluble in water. It is nonpolar and water is polar, so they are incompatible.
4.  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$  is a large molecule, but since it has many  $-\text{OH}$  groups, it can form lots of hydrogen bonds with water. It is therefore very soluble in water.
5.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is completely soluble in  $\text{C}_6\text{H}_6$  or any other nonpolar solvent.