Unit One Part 5: intermolecular forces

- Bond polarisation and molecular dipoles
- Intermolecular forces (attraction / repulsion between molecules)
- Relative strengths of these forces
- Briefly look at each of the different intermolecular forces
Intermolecular forces

- Bonding within a molecule obviously has a great effect on its properties.
- But as important is the forces between molecules - **intermolecular forces**.
- The 3 isomers above have different bp due to different intermolecular forces.

- **pentane**: bp 36.2°C
- **2-methylbutane**: bp 28°C
- **2,2-dimethylpropane**: bp 9.6°C

- **2-methylpropan-2-ol (tert-butanol)**: \( \text{C}_4\text{H}_{10}\text{O} \), mp 26°C
- **Diethyl ether**: \( \text{C}_4\text{H}_{10}\text{O} \), mp –116°C
Dipoles and dipole moments

- We have seen that different atoms attract electrons by varying amounts.
- The greater the difference the larger the **bond dipole**.
- **Molecular dipole** is the sum of the **bond dipoles**.

- A molecule with polar bonds and a molecular dipole is **polar**.
- A molecule that has no overall molecular dipole is **nonpolar**.
Inductive effects

- Bond dipoles can induce a small dipole into neighbouring bonds.
- Here chlorine is an electron-withdrawing group.
- Alkyl groups are electron-donating groups $H_3C\rightarrow C$.
- Effect on chemistry is shown with the strength of carboxylic acids.

\[
\begin{align*}
\text{H}_3\text{C} &\rightarrow \text{C} \\
\text{H}_3\text{C} &\rightarrow \text{C} \\
\text{H}_3\text{C} &\rightarrow \text{C}
\end{align*}
\]

- Lower the $pK_a$ value the easier it is to remove $H$.

\[
\begin{align*}
\text{H}_3\text{C} &\rightarrow \text{O} \rightarrow \text{H} \\
\text{Cl} &\rightarrow \text{O} \rightarrow \text{H} \\
\text{Cl} &\rightarrow \text{O} \rightarrow \text{H} \\
\text{Cl} &\rightarrow \text{O} \rightarrow \text{H}
\end{align*}
\]

\[
\begin{align*}
pK_a &= 4.75 \\
pK_a &= 2.85 \\
pK_a &= 1.48 \\
pK_a &= 0.70
\end{align*}
\]
**Intermolecular forces**

- **Intermolecular forces** - affect physical properties (mp, bp etc.)
- **Intramolecular forces** - govern chemical reactions

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Typical Energy (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic-ionic (ionic bond)</td>
<td>250</td>
</tr>
<tr>
<td>carbon-containing covalent bond</td>
<td>350</td>
</tr>
<tr>
<td>oxygen-hydrogen covalent bond</td>
<td>460</td>
</tr>
<tr>
<td>hydrogen (H-) bond</td>
<td>20</td>
</tr>
<tr>
<td>ion-dipole</td>
<td>15</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>2</td>
</tr>
<tr>
<td>London (dispersion)</td>
<td>2</td>
</tr>
</tbody>
</table>

**Diagram Explanation**

- **Covalent bond (strong)**: The strong covalent bond is indicated by a solid line between the atoms. This bond is formed by the sharing of electrons between two atoms, resulting in a strong interaction.

- **Intermolecular attraction (weak)**: The weak intermolecular attraction is indicated by a dotted line between the molecules. This attraction is weaker than the covalent bond and includes various types of forces such as hydrogen bonds, ion-dipole, dipole-dipole, and London dispersion forces. The typical energies associated with these forces are listed in the table above.
Ion-Dipole Forces

- Charged ion (+ / −) interacts with oppositely charged part of molecule with a permanent dipole (δ− / δ +)
- Ion-dipole interactions are a strong intermolecular force (15 kJmol⁻¹)
- Explains how water dissolves salts (ionic compounds)
- Organic molecules can interact in the same way
Dipole-Dipole forces

- Molecules with **permanent dipoles** orient themselves to match charges.
- These interactions are quite weak (>> 2kJmol⁻¹).
- Thus polar molecules can interact with one another & mix (miscible).

- Can have profound effect on boiling points.

**Examples:**
- **Propanone** (Acetone): Mol Wt. 58; bp 56°C. **Permanent dipole**.
- **Butane**: Mol Wt. 58; bp -0.6°C. **No dipole**.
Hydrogen Bonding

- Special example of dipole-dipole attraction
- Requires H in highly polar bond (joined to O, N etc.) - H-bond donor
- Requires lone-pair on electronegative atom (O, N & F) - H-bond acceptor
- Strongest intermolecular force (>> 20kJmol⁻¹)

- Explains water's abnormally high mp & bp
  H₂O (MW=18), bp 100°C
  H₂S (MW=34): bp –60°C
  CH₄ (MW=16): bp –162°C
Hydrogen bonding II

Carboxylic acids form extensive H-bond arrays
Acetic acid has two polarised bond and forms dimers readily

Methanol has only one H attached to O
It can only form one Hydrogen bond
Its bp is lower than water (62°C)

H-bonding explains why acetic acid is so soluble in water
Hydrogen bonding in biology

**H-bonding** occurs between two different heteroatoms

- Interaction between **C=O** & **N–H** important in protein secondary structure
- Whilst **N** & **O** are important **H-bond acceptors** in DNA base pairs

![Diagram of hydrogen bonding](image)

![Molecular structures](image)
London (dispersion or van der Waals) forces

- London forces are weak forces found in all molecules
- Electrons move to create small, temporary dipole
- This dipole can induce a dipole into nearby molecules & thus create attraction

• Bigger the molecules surface area the greater the London force / dipole
London forces II

- Longer the chain the bigger the possible dipole & greater the attraction
- More branching in an alkane decreases relative surface area & reduces London forces

methane
CH$_4$ (MW=16)
mp $-182^\circ$C; bp $-164^\circ$C
gas at rt

hexane
C$_6$H$_{14}$ (MW=86)
mp $-95^\circ$C; bp $-69^\circ$C
liquid at rt

eicosane
C$_{20}$H$_{42}$ (MW=282)
mp 36°C; bp 343°C
solid at rt

pentane
bp 36°C

2,2-dimethylpropane
bp 9.5°C
### Solvation

- **Solvation** - interaction between molecule and the solvent molecules
- **Hydrophobic** - molecules/motifs are insoluble in water (e.g. greasy chains)
- **Hydrophilic** - molecules / functional groups are soluble in water (e.g. -OH)
- Polar materials dissolve in polar solvents

<table>
<thead>
<tr>
<th>compound</th>
<th>bp (°C)</th>
<th>solubility (g/100mL H₂O)</th>
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<tbody>
<tr>
<td>propanol</td>
<td>CH₃CH₂CH₂OH</td>
<td>97</td>
</tr>
<tr>
<td>butanol</td>
<td>CH₃(CH₂)₂CH₂OH</td>
<td>117</td>
</tr>
<tr>
<td>propanoic acid</td>
<td>CH₃CH₂CO₂H</td>
<td>141</td>
</tr>
<tr>
<td>butanoic acid</td>
<td>CH₃(CH₂)₂CO₂H</td>
<td>164</td>
</tr>
<tr>
<td>hexanoic acid</td>
<td>CH₃(CH₂)₄CO₂H</td>
<td>205</td>
</tr>
<tr>
<td>decanoic acid</td>
<td>CH₃(CH₂)₈CO₂H</td>
<td>–</td>
</tr>
</tbody>
</table>
Solvation II

- Does glucose dissolve in water or hexanes?
  - **Hydroxyl** groups are polar & **H-bond** to water - so soluble in water

- What about DEET, an insect repellant?
  - Large nonpolar **aromatic ring**, polar amide but no H-bonding capability
  - So better in ethanol than water
Overview

What have we learnt?
- That molecules are attracted to each other
- Many different forms of attraction
- These forces have profound effects on physical properties

What's next?
- Looking at chemical reactions (yippee)
- Looking at reaction profiles (boo)
- Shapes of molecules (the return of...)