Chapter 1

Dipole Moments, Molecular Polarity and Intermolecular Forces
Polarity of Molecules

For a molecule to be polar, it must

*have polar bonds, and*

*have an unsymmetrical shape*

Polarity affects the intermolecular forces of attraction

*and therefore affects boiling points and solubilities*

Nonbonding pairs affect molecular polarity.
Net dipole moment

Polar bond

No net dipole moment

Net dipole moment
CH$_4$  
NH$_3$  
H$_2$O

electrostatic potential map for methane  
electrostatic potential map for ammonia  
electrostatic potential map for water

red $<$ orange $<$ yellow $<$ green $<$ blue

most negative electrostatic potential  
most positive electrostatic potential
Predicting Polarity of Molecules

1. Draw the Lewis structure and determine the molecular geometry.

2. Determine whether the bonds in the molecule are polar.

3. Determine whether the polar bonds add together to give a net dipole moment.
Molecular Polarity

chloromethane $\mu = 1.87$ D

water $\mu = 1.85$ D

ammonia $\mu = 1.47$ D

$\mu = 0.234$ D
Attractive Forces

Particles are attracted to each other by electrostatic forces.

The strength of the attractive forces depends on the kind(s) of particles.

The stronger the attractive forces between the particles, the more they resist moving.

The strength of the attractions between particles of a substance determines its physical state.
Kinds of Attractive Forces

Dispersion Forces between Molecules
Temporary polarity in molecules due to unequal electron distribution

Dipole–Dipole Attractions between Molecules
Permanent polarity in molecules due to their structure

Hydrogen Bonds between Molecules
An especially strong dipole–dipole attraction resulting from the attachment of H to an extremely electronegative atom

Ion–Dipole Attractions - Not Intermolecular
Between mixtures of ionic compounds and polar compounds (esp. aqueous solutions)
Some molecules are considered *nonpolar* because of the atoms which they contain and the arrangement of these atoms in space.

But these molecules can all be “*condensed.*”
Origin of Instantaneous Dipoles

The \( \delta^+ \) charge attracts electrons. The \( \delta^- \) charge repels electrons.
Size of the Induced Dipole

The magnitude of the induced dipole depends on several factors:

**Polarizability of the electrons**

**Volume of the electron cloud**

- larger molar mass
  - ⇒ more electrons
  - ⇒ larger electron cloud
  - ⇒ increased polarizability
  - ⇒ stronger attractions

Larger molecules have more electrons, leading to increased polarizability.
Size of the Induced Dipole

Shape of the molecule

more surface-to-surface contact ⇒ larger induced dipole ⇒ stronger attraction

Molecules that are flat have more surface interaction than spherical ones.
**Effect of Molecular Size on Magnitude of Dispersion Force**

As the molar mass increases, the number of electrons increases. Therefore, the strength of the dispersion forces increases. The stronger the attractive forces between the molecules, the higher the boiling point.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Radius</th>
<th>Molar Mass</th>
<th>B.P.(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>31</td>
<td>4</td>
<td>4.2</td>
</tr>
<tr>
<td>Ne</td>
<td>38</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>Ar</td>
<td>71</td>
<td>40</td>
<td>87</td>
</tr>
<tr>
<td>Kr</td>
<td>88</td>
<td>84</td>
<td>120</td>
</tr>
<tr>
<td>Xe</td>
<td>108</td>
<td>131</td>
<td>165</td>
</tr>
<tr>
<td>Rn</td>
<td>120</td>
<td>222</td>
<td>211</td>
</tr>
</tbody>
</table>
Boiling Points of Straight Chain Alkanes
NonPolar Molecules

Boiling point (°C) vs. Molar mass (g/mol)

- $n$-Nonane ($C_9H_{20}$)
- $n$-Octane ($C_8H_{18}$)
- $n$-Heptane ($C_7H_{16}$)
- $n$-Hexane ($C_6H_{14}$)
- $n$-Pentane ($C_5H_{12}$)
Effect of Molecular Shape on Size of Dispersion Force

A larger surface-to-surface contact between molecules results in stronger dispersion force attractions and a higher boiling point.
Practice – Choose the Substance in Each Pair with the Higher Boiling Point

a) CH₄

b) C₆H₁₂
Dipole–Dipole Attractions

Some molecules are inherently **polar** because of the atoms which they contain and the arrangement of these atoms in space.

A crude representation of a polar molecule

\[ \text{H}_2\text{O} \quad \text{NH}_3 \quad \text{CH}_2\text{O} \quad \text{HCl} \]
Dipole–Dipole Attractions

Polar molecules have a permanent dipole because of bond polarity and shape

1) dipole moment
2) as well as the always present induced dipole

The permanent dipole adds to the attractive forces between the molecules
### Effect of Dipole–Dipole Attraction on Boiling and Melting Points

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molar mass</th>
<th>Structure</th>
<th>b.p.</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>formaldehyde</td>
<td>CH₂O</td>
<td>30.03</td>
<td><img src="image1" alt="Structure" /></td>
<td>-19.5°</td>
<td>-92°</td>
</tr>
<tr>
<td>ethane</td>
<td>C₂H₆</td>
<td>30.07</td>
<td><img src="image2" alt="Structure" /></td>
<td>-88°</td>
<td>-172°</td>
</tr>
</tbody>
</table>
Determine if dipole–dipole attractions occur between CH₂Cl₂ molecules

**Formula**: 

- **Lewis Structure**: [Diagram]
  - 4 bonding areas
  - no lone pairs
  - tetrahedral shape

**Bond Polarity**

- **Cl—C**: 3.0–2.5 = 0.5
  - polar
- **C—H**: 2.5–2.1 = 0.4
  - nonpolar

**Molecule Polarity**

- Polar molecule; therefore dipole–dipole attractions do exist
Hydrogen Bonding

When a very electronegative atom is bonded to hydrogen, it strongly pulls the bonding electrons toward it:

\[ \text{O–H, N–H, F–H} \]

Because hydrogen has no other electrons, when its electron is pulled away, the nucleus becomes deshielded, exposing the H proton.

The exposed proton acts as a very strong center of positive charge.
H-Bonding in Water

Hydrogen Bonds
Hydrogen Bonding and Boiling Points

Period

Boiling Point (°C)

Group IVA
Group VA
Group VIA
Group VIIA

H₂O
H₂Te

HF
H₂Se

NH₃
H₂S

CH₄
SiH₄

GeH₄

AsH₃
HBr

SbH₃
HI

SnH₄

H₂S
H₂Se
### Effect of Hydrogen-Bonding on Boiling and Melting Points

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molar mass</th>
<th>Structure</th>
<th>Structure</th>
<th>b.p.</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>C₂H₆O</td>
<td>46.07</td>
<td><img src="image" alt="Ethanol Structure" /></td>
<td><img src="image" alt="Ethanol Structure" /></td>
<td>78.2º</td>
<td>-114.1º</td>
</tr>
<tr>
<td>dimethyl ether</td>
<td>C₂H₆O</td>
<td>46.07</td>
<td><img src="image" alt="Dimethyl Ether Structure" /></td>
<td><img src="image" alt="Dimethyl Ether Structure" /></td>
<td>-22º</td>
<td>-138.5º</td>
</tr>
</tbody>
</table>
One of these compounds is a liquid at room temperature (the others are gases). Which one and why?

Because only hydrogen peroxide has the additional very strong H-bond additional attractions, its intermolecular attractions will be the strongest. We therefore expect hydrogen peroxide to be the liquid.
All Molecules

Polar Molecules

Molecules containing O-H, N-H, or F-H Bonds

Hierarchy of Intermolecular Forces

Dispersion forces
Dipole forces
H-bonding
Melting Points of n-Alkanes

The graph shows the relationship between the number of carbon atoms and the melting point (°C) of n-alkanes. The melting points increase as the number of carbon atoms increases. There is a distinction between even and odd numbers of carbon atoms, with odd numbers generally having slightly lower melting points than even numbers at the same carbon content.

- **Even numbers**: Melting points decrease slightly with each additional carbon atom.
- **Odd numbers**: Melting points decrease more significantly with each additional carbon atom compared to even numbers.

The graph illustrates this trend with data points and trend lines for both even and odd numbers of carbon atoms.
## Boiling Points of Other Organic “Families”

<table>
<thead>
<tr>
<th>Alkanes</th>
<th>Ethers</th>
<th>Alcohols</th>
<th>Amines</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_3 )</td>
<td>( \text{CH}_3\text{OCH}_3 )</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} )</td>
<td>( \text{CH}_3\text{CH}_2\text{NH}_2 )</td>
</tr>
<tr>
<td>-42.1°</td>
<td>-23.7°</td>
<td>+78°</td>
<td>+16.6°</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>( \text{CH}_3\text{OCH}_2\text{CH}_3 )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 )</td>
</tr>
<tr>
<td>-0.5°</td>
<td>+10.8°</td>
<td>+97.4°</td>
<td>+47.8°</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 )</td>
<td>( \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 )</td>
</tr>
<tr>
<td>+36.1°</td>
<td>+34.5°</td>
<td>+117.3°</td>
<td>+77.8°</td>
</tr>
</tbody>
</table>
Solubility
Solubility

When one substance (solute) dissolves in another (solvent) it is said to be

When one substance does not dissolve in another it is said to be

The solubility of one substance in another depends on two factors - nature’s tendency toward mixing, and the solute and solvent.
Attractive Forces Acting Between Ions & Molecules

Pure **Electrostatic Attractions** - chiefly ionic compounds

![Diagram of electrostatic attractions](image)

**Dipole-dipole attractions** - chiefly between molecules

![Diagram of dipole-dipole attractions](image)

**Dispersion Forces** Very weak, due to a temporary shift in electron distribution dependent on the size of the molecule

![Diagram of dispersion forces](image)
What happens when you dissolve an ionic compound in water??

What happens when you dissolve a polar molecule in water??
What Happens When an Ionic Compound Dissolves in Water?
What Happens When a Polar Covalent Compound Dissolves in Water?

**Solvation step:** Formation of attractive forces between solvent particles and solute particles

**dipole-dipole attractions**
What happens when you try to dissolve a nonpolar molecule in water?
What happens when you try to dissolve a nonpolar molecule in water??

Non polar solvents, such as ethanol, carbon tetrachloride, ether, and hexane, are also commonly used to dissolve nonpolar solutes, such as grease and oils.
General Solubility Rule: “Like Dissolves Like”

Polar solutes form solutions with polar solvents.

Nonpolar solutes form solutions with nonpolar solvents.
# Selected Polar and Nonpolar Solvents

<table>
<thead>
<tr>
<th>POLAR SOLVENTS</th>
<th>NONPOLAR SOLVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>water, H$_2$O</td>
<td>hexane, C$<em>6$H$</em>{14}$</td>
</tr>
<tr>
<td>methanol, CH$_3$OH</td>
<td>heptane, C$<em>7$H$</em>{16}$</td>
</tr>
<tr>
<td>ethanol, C$_2$H$_5$OH</td>
<td>toluene, C$_7$H$_8$</td>
</tr>
<tr>
<td>acetone, C$_3$H$_6$O</td>
<td>carbon tetrachloride, CCl$_4$</td>
</tr>
<tr>
<td>methyl ethyl ketone, CH$_3$CH$_2$C(O)CH$_3$</td>
<td>chloroform, CHCl$_3$</td>
</tr>
<tr>
<td>formic acid, HCOOH</td>
<td>methylene chloride, CH$_2$Cl$_2$</td>
</tr>
<tr>
<td>acetic acid, CH$_3$COOH</td>
<td>ethyl ether, CH$_3$CH$_2$OCH$_2$CH$_3$</td>
</tr>
</tbody>
</table>
## Solubility* of a Series of Alcohols in Water and Hexane

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Model</th>
<th>Solubility in Water</th>
<th>Solubility in Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OH</td>
<td><img src="image1" alt="Model" /></td>
<td>∞</td>
<td>1.2</td>
</tr>
<tr>
<td>(methanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CH(_2)OH</td>
<td><img src="image2" alt="Model" /></td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>(ethanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)(CH(_2))_2OH</td>
<td><img src="image3" alt="Model" /></td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>(propanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)(CH(_2))_3OH</td>
<td><img src="image4" alt="Model" /></td>
<td>1.1</td>
<td>∞</td>
</tr>
<tr>
<td>(butanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)(CH(_2))_4OH</td>
<td><img src="image5" alt="Model" /></td>
<td>0.30</td>
<td>∞</td>
</tr>
<tr>
<td>(pentanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)(CH(_2))_5OH</td>
<td><img src="image6" alt="Model" /></td>
<td>0.058</td>
<td>∞</td>
</tr>
<tr>
<td>(hexanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Expressed in mol alcohol/1000 g solvent at 20°C.