Solids, liquids and gases

- Solids, liquids, and gases are held together by intermolecular forces.
- Intermolecular forces occur between molecules, not within molecules (as in bonding).
- When a molecule changes phases it remains intact – the molecule does not change, just the forces among the molecules around it.

<table>
<thead>
<tr>
<th>State</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (0°C, 1 atm)</td>
<td>0.9168</td>
</tr>
<tr>
<td>Liquid (25°C, 1 atm)</td>
<td>0.9971</td>
</tr>
<tr>
<td>Gas (400°C, 1 atm)</td>
<td>$3.26 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Densities of the Three States of Water
Intermolecular forces determine:

Boiling Point
Vapor Pressure
Viscosity (measure of a liquid’s resistance to flow)
Surface Tension (resistance of a liquid to an increase in its surface area)

Stronger forces require more energy to disrupt intermolecular interactions
There are two types of intermolecular forces

- Intermolecular forces are determined by the nature of the molecules:
  - Non-polar molecules experience *London dispersion forces*
  - Polar molecules experience *dipole-dipole forces*
- A special case of dipole-dipole forces is *hydrogen bonding*...more later
London Dispersion Forces

• In molecules without a permanent dipole moment, it is possible to induce an “instantaneous” dipole moment.
• The interaction is weak and short-lived, but can be very significant for large molecules (often more than dipole-dipole).
Bromine

- $\text{Br}_2$: m.p., -7 °C; b.p., 59 °C.
- **Molecular** substances have relatively low melting and boiling points because the molecules are held together by fairly weak forces.
Types of Intermolecular Forces

**Dipole-dipole forces**

- Polar molecules align to put positive and negative poles near each other.
- Fall off rapidly over distance – so are relatively unimportant in the gas phase.
- Occur in molecules with polar bonds and dipole moments.
- Typically 5-25 kJ/mol.
Hydrogen Bonding

A special type of dipole-dipole force:
• Dipole-dipole forces are very strong when N-H, O-H or F-H bonds are present.
• Why?
  • These bonds are very polar (electronegativity differences are large)
  • The H is small so the dipoles can get very close together.

Even though the strength of one H bond may be small, the combined strength of many H bonds can be large.
Boiling Points are high in H-bonded liquids

Exceptions

O, N, F → Small sizes, Large electronegativities: Strong H-bonds
Problem: In which of the following molecules does hydrogen bonding occur? Draw the hydrogen bonds where appropriate in the molecules.

a) C₃H₈  
b) C₂H₅OH  
c) Glycine: H₂NCH₂COOH

Plan: We examine each structure to see if F, N, or O is present, and if hydrogen can be bonded to them.

Solution:

a) for C₃H₈, only C-C and C-H bonds exist. **No** hydrogen bonds can be formed!

```
  H   H   H
 /     /     /
H ── C ── C ── C ── H
  |     |     |
H   H   H
```

b) for C₂H₅OH, the H covalently bound to the oxygen can interact with the pair of electrons on the oxygen of another molecule **to form a strong hydrogen bond**. It can also hydrogen bond with water molecules...
b) Ethanol:
Covalent Bonding and H bonding in the Structure of Deoxyribonucleic Acid (DNA)

Adenine (A) ↔ Thymine (T)

Guanine (G) ↔ Cytosine (C)
## Comparison of the Energies Associated with Bonding (Intramolecular) Forces and Intermolecular Forces

<table>
<thead>
<tr>
<th>Force</th>
<th>Model</th>
<th>Basis of Attraction</th>
<th>Energy (kJ/mol)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intramolecular</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic</td>
<td></td>
<td>Cation–anion</td>
<td>400–4000</td>
<td>NaCl</td>
</tr>
<tr>
<td>Covalent</td>
<td></td>
<td>Nuclei–shared e(^{-}) pair</td>
<td>150–1100</td>
<td>H–H</td>
</tr>
<tr>
<td>Metallic</td>
<td></td>
<td>Cations–delocalized electrons</td>
<td>75–1000</td>
<td>Fe</td>
</tr>
<tr>
<td>Intermolecular</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion-dipole</td>
<td></td>
<td>Ion charge–dipole charge</td>
<td>40–600</td>
<td>Na(^{+})--OH</td>
</tr>
<tr>
<td>H bond</td>
<td></td>
<td>Polar bond to H–dipole charge (high EN of N, O, F)</td>
<td>10–40</td>
<td>·········</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td></td>
<td>Dipole charges</td>
<td>5–25</td>
<td>I–Cl····I–Cl</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td></td>
<td>Ion charge–polarizable e(^{-}) cloud</td>
<td>3–15</td>
<td>Fe(^{2+})--O(_2)</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td></td>
<td>Dipole charge–polarizable e(^{-}) cloud</td>
<td>2–10</td>
<td>H–Cl····Cl–Cl</td>
</tr>
<tr>
<td>Dispersion (London)</td>
<td></td>
<td>Polarizable e(^{-}) clouds</td>
<td>0.05–40</td>
<td>F–F····F–F</td>
</tr>
</tbody>
</table>
Note: There can be more than one type of intermolecular interaction between molecules or ions.

- Tetramethylammonium ion
- Nitrate ion

Ion-ion dispersion

- Ammonium ion
- Nitrate ion

Hydrogen-bonding dispersion
Problem: Select the substance with the higher boiling point in each pair:

a) CH₃Cl or CH₃OH
b) CH₃CH₂OH or C₂H₄(OH)₂

Plan: Examine the formulas and structures to determine the types of forces involved: Are ions present? Are the molecules polar or nonpolar? Is F, O, or N bound to H? Do the molecules have different masses or shapes?

Remember:

a) Bonding (intramolecular) forces are stronger than intermolecular forces.

b) Hydrogen bonding is a strong type of dipole-dipole force.

c) Dispersion forces are decisive when the major difference is molar mass or molecular shape.
Solutions:

a) CH₃Cl (methyl chloride, MM=50.48g/mol) and CH₃OH (methanol, MM=32.04g/mol) are both polar molecules. CH₃OH has an O-H bond, so it can form hydrogen bonds, which are stronger than the dipole-dipole forces that exist between the molecules in CH₃Cl. CH₃OH will have the greater boiling point.

Check: CH₃Cl (b.p. = -24.22°C) and CH₃OH (b.p. = 64.65°C)

b) CH₃CH₂OH (ethyl alcohol, MM=46.07g/mol) and HOCH₂CH₂OH (ethylene glycol, MM=64.07g/mol) both contain an O-H group, but ethylene glycol is a di-hydroxy alcohol so it can have twice the hydrogen bonding - it will have the higher boiling point.

Check: CH₃CH₂OH (b.p. = 78.5°C) and HOCH₂CH₂OH (b.p. = 290°C)
What Affects Solubility?

- **Structure**
  - Whether a solute is “hydrophobic” or “hydrophilic”

- **Pressure**
  - Little effect on solids or liquids
  - LARGE effect on gases

- **Temperature**
  - Tricky to predict with solids and liquids (though the process of *dissolving* is always faster with higher temperature).
  - Gas solubility always decreases with increasing temperature (think warm soda – *yuck!*).
Structure Affects Solubility

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Model</th>
<th>Water</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH (methanol)</td>
<td></td>
<td>∞</td>
<td>0.12</td>
</tr>
<tr>
<td>CH₃CH₂OH (ethanol)</td>
<td></td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃(CH₂)₂OH (propanol)</td>
<td></td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃(CH₂)₃OH (butanol)</td>
<td></td>
<td>0.11</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃(CH₂)₄OH (pentanol)</td>
<td></td>
<td>0.030</td>
<td>∞</td>
</tr>
<tr>
<td>CH₃(CH₂)₅OH (hexanol)</td>
<td></td>
<td>0.0058</td>
<td>∞</td>
</tr>
</tbody>
</table>

* Expressed in mol alcohol/100 g solvent at 20°C.
Hydration shells around an aqueous ion
→ more charge density (charge/size ratio of ion) results in greater hydration
Effect of Structure on Solubility...

Nonpolar, fat-soluble (builds up in fatty tissues – pros and cons!)

Polar, water-soluble (must be consumed regularly – pros and cons!)

Other examples:
*Vitamins D, E, and K* (fat soluble); *Vitamin B* (water-soluble)
*DDT* – pesticide (fat soluble)
*Dioxins* – group of molecules, herbicides and pollutants (fat soluble)
*BaSO₄* – gastroenterology, enhances X-rays (insoluble)
Problem: Predict which solvent will dissolve more of the given solute.

(a) Sodium Chloride
   in methanol (CH$_3$OH) or in propanol (CH$_3$CH$_2$CH$_2$OH).

(b) Ethylene glycol (HOCH$_2$CH$_2$OH)
   in water or in hexane (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$).

(c) Diethyl ether (CH$_3$CH$_2$OCH$_2$CH$_3$)
   in ethanol (CH$_3$CH$_2$OH) or in water.

Plan: Examine each solute and solvent to determine which intermolecular forces will be active.

A solute tends to be more soluble in a solvent that has the same type of intermolecular forces active.
**Problem:** Predict which solvent will dissolve more of the given solute.

(a) Sodium Chloride in methanol \((\text{CH}_3\text{OH})\) or in propanol \((\text{CH}_3\text{CH}_2\text{CH}_2\text{OH})\).

**Solution:**

(a) **Methanol** - NaCl is an ionic compound that dissolves through ion-dipole forces. Both methanol and propanol contain a polar O-H group, but propanol’s longer hydrocarbon chain would interact only weakly with the ions and be less effective in stabilizing the ions.
Predicting Relative Solubilities of Substances

**Problem:** Predict which solvent will dissolve more of the given solute.

**(b) Ethylene glycol** \((\text{HOCH}_2\text{CH}_2\text{OH})\) in **water** or in **hexane** \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)\).

**Solution:**
**(b) Water** - Ethylene glycol has two O-H groups and is stabilized by extensive H-bonding in water.

**(c) Diethyl ether** \((\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)\) in **ethanol** \((\text{CH}_3\text{CH}_2\text{OH})\) or in **water**.

**Solution:**
**(c) Ethanol** - Diethyl ether shows both dipolar and dispersion intermolecular forces and could form H bonds to both water and ethanol. The ether would be more soluble in ethanol because solvation in water must disrupt many more strong H-bonding interactions.
Increase in gas solubility with increased pressure

At equilibrium

Increase in $P$ (and $r$)

Increase in $[\text{gas dissolved}]$
Henry’s Law

The amount of gas dissolved in a solution is directly proportional to the pressure of the gas above the solution.

\[ P = k_H X \]

- \( P \rightarrow \) partial pressure of the gaseous solute above the solution
- \( X \rightarrow \) mole fraction of the dissolved gas
- \( k_H \rightarrow \) a constant characteristic of a particular solution

Requirement:
This law holds only if there is no chemical reaction between the solute and the solvent and if the solution is fairly dilute.

For all gases: \( \Delta H_{\text{solute}} \approx 0 \), so \( \Delta H_{\text{soln}} < 0 \)

Gas solubility always decreases with increasing \( T \)!
Henry’s Law - Lake Nyos in Cameroon

CO₂ buildup in colder, denser water layers near lake’s bottom (high pressure, large mole fraction); “overturn” in 1986 sent water supersaturated with CO₂ to the surface and released an enormous amount of CO₂ into the area, suffocating thousands of humans and animals.
Changes of State

• You need to add energy to a substance to melt or vaporize it. How much energy you need is determined by the intermolecular forces.
• The energy needed to melt a solid is called the enthalpy or heat of fusion: $\Delta H_{\text{fus}}$
• When molecules escape from the liquid state to form a gas, the process is called vaporization (evaporation). $\Delta H_{\text{vap}} = \text{energy needed to vaporize 1 mol of liquid at 1 atm pressure}$.
• Not all substances need to pass from solid to liquid to gas. Some substances can go from solid directly to gas. This is called sublimation.
Changes of State

• Let’s look at the one “Phase transition”: liquid to gas
• Also known as “boiling” or “evaporation”.
• Molecules in the liquid phase gain enough kinetic energy to overcome the intermolecular forces and “escape” into the gas phase.
• We use vapor pressure as a measure of a liquid’s intermolecular forces.
Vapor Pressure

At equilibrium, Evaporation rate = Condensation rate

The pressure of the vapor at equilibrium is called the Vapor Pressure ($P_{vap}$) of the liquid (or solid) – think of this as the number of gas molecules pushing down on the liquid or solid
• If $P_{vap}$ is large, the substance is called *volatile*
• As intermolecular forces increase, $P_{vap}$ decreases
More volatile substances have higher $P_{vap}$ at lower T (more molecules in the vapor phase)
Changes of State - Definitions

Melting point:
- The point at which the vapor pressures of the solid and liquid are identical.
- The solid and liquid states are both present
- “Normal”: total $P_{vap} = 1$ atm

Boiling point:
- In general, boiling occurs when the $P_{vap}$ of a liquid becomes equal to the pressure of its environment
- “Normal”: temperature at which $P_{vap} = 1$ atm
Changes of state are sensitive to pressure

Boiling occurs when the vapor pressure of a liquid becomes equal to the pressure of its environment.

In the mountains, atmospheric pressure is reduced, so water boils at a lower temperature. (Less heat is required to achieve $P_{\text{vap}} = P_{\text{atm}}$)

see Figure 16.53
Phase diagrams are important "road maps" for understanding the effects of temperature and pressure on a substance.
**Phase Diagram Definitions**

- **Critical temperature**: the temperature above which a vapor cannot be liquefied, no matter what pressure is applied.
- **Critical pressure**: the pressure required to produce liquefaction *at* the critical temperature.
- Together they define the **critical point**: beyond this point the transition from one state to another involves neither true liquid nor vapor.
Phase Diagrams for CO₂ and H₂O

A) CO₂
- Critical point: (31°C, 73 atm)
- Melting/Freezing
- Sublimation/Deposition
- Vaporization/Condensation
- Triple point: (-57°C, 5.1 atm)

B) H₂O
- Critical point: (374°C, 218 atm)
- Triple point: (0.01°C, 0.006 atm)
Phase Changes for Water and their Enthalpies

- Condensation: $-\Delta H_{\text{vap}}^{0} = -40.7 \text{ kJ/mol}$
- Vaporization: $\Delta H_{\text{vap}}^{0} = 40.7 \text{ kJ/mol}$
- Freezing: $-\Delta H_{\text{fus}}^{0} = -6.02 \text{ kJ/mol}$
- Melting: $\Delta H_{\text{fus}}^{0} = 6.02 \text{ kJ/mol}$
Phase Changes for Water and their Enthalpies

- Condensation
  - $-\Delta H_{\text{vap}}^0 = -40.7 \text{ kJ/mol}$

- Vaporization
  - $\Delta H_{\text{vap}}^0 = 40.7 \text{ kJ/mol}$

- Freezing
  - $-\Delta H_{\text{fus}}^0 = -6.02 \text{ kJ/mol}$

- Melting
  - $\Delta H_{\text{fus}}^0 = 6.02 \text{ kJ/mol}$
Phase Changes for Water and their Enthalpies

Gas

\[ \Delta H^0_{\text{sub}} \]

Sublimation

Solid

\[ -\Delta H^0_{\text{sub}} \]

Deposition
Liquids

- Many liquids have the tendency to bead on a surface.
- This is the result of surface tension – the liquid’s resistance to an increase in surface area.
- Large intermolecular forces lead to high surface tension.
Surface tension: the resistance of a liquid to an increase in surface area; “surface” can be vapor/solid; molecule at the surface only attracted by molecules next to and below it.
Shape of the Water or Mercury Meniscus in Glass

A: Adhesive

B: Cohesive
Capillary Action

• Polar liquids also exhibit capillary action: the spontaneous rising of liquid up a narrow tube.

• This is the result of cohesive (intermolecular) and adhesive (liquid / container) forces at work.
  – The liquid “wets” the surface → increases surface area → liquid pulls itself up.
Surfactants: Polar + Non-Polar Hybrids

Polar “head” - CO$_2^-$ as in soap
Non-polar “tail” - CH$_2$-CH$_2$-CH$_2^-$ as in industrial detergents

Air

Air-water interface

Weak non-covalent forces

Polar liquid

**Surfactant:** surface acting agent; lowers the surface tension of a liquid (easier spreading)
Why is water so awesome?

• (Near) universal solvent
  – The high polarity (and therefore, hydrogen bonding power) of water means it can dissolve so many compounds – ionic compounds, polar, non-ionic compounds and even non-polar gases.
Why is water so awesome?

• Thermal properties
  – Water has a high heat capacity (higher than almost any liquid). High intermolecular forces mean water can absorb a lot of heat before it boils. This allows the earth to remain at a steady temperature.
  – Water has a high heat of vaporization which gives it enormous cooling power. Example:

  *Adding 4 kJ of heat to 1000g of water causes the temperature to rise 1 °C, but only 2g of that water has to evaporate to keep the remaining 998g at a constant temperature.*
Why is water so awesome?

- Surface properties
  - High surface tension and high “capillarity” (both results of hydrogen bonding) are critical to plant life (land and aquatic).
Why is water so awesome?

• Density of solid and liquid water
  – Because solid water (ice) is less dense than liquid water (as a result of hydrogen bonding), ice floats on water. This protects aquatic life, erodes rocks, but sometimes freezes your pipes...