Chapter Map

Why particles spread out (disperse)

Structure of liquid water (Section 3.3)

Why ethanol and water mix

Solute, solvent, and solution (Section 4.2)

Hydrophobic and hydrophilic substances and groups

Structure of triglycerides

Making soap from triglycerides

Why soaps and detergents work

Structure of typical detergent

Types of compounds, types of attractions and particles (Section 14.2)

Describe hydrogen bonds (Section 14.3)
Why Changes Happen

- Consider a system that can switch back and forth between two states, A and B, such as between solid carbon dioxide and gaseous carbon dioxide.
Why Changes Happen

- Probability helps us to predict that the system will shift to state B if state B has its particles and energy more dispersed, leading to more ways to arrange the particles and energy in the system.

<table>
<thead>
<tr>
<th>State A</th>
<th>State B</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2(s)</td>
<td>CO_2(g)</td>
</tr>
<tr>
<td>Less dispersed (spread out)</td>
<td>More dispersed (spread out)</td>
</tr>
<tr>
<td>Fewer ways to arrange particles and energy</td>
<td>More ways to arrange particles and energy</td>
</tr>
<tr>
<td>Less probable</td>
<td>More probable</td>
</tr>
</tbody>
</table>
### 9-Point Universe

<table>
<thead>
<tr>
<th>Solid-like states</th>
<th>4 possible arrangements of the red particles produce a less dispersed, solid-like state.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-like states</td>
<td>122 possible arrangements produce a more dispersed, gas-like state.</td>
</tr>
</tbody>
</table>

![Diagram of particle arrangements]
In a 9-point universe, 96% of the arrangements of 4 particles are gas-like.

In a 16-point universe, 99.5% of the arrangements of 4 particles are gas-like.

Therefore, an increase in the number of possible positions leads to an increase in the probability that the system will be in the more dispersed, gas-like state.

In real systems, there are huge numbers of particles in huge numbers of positions, so there is an extremely high probability that the systems shift to a more dispersed, gas-like state.
General Statement

• Changes tend to take place to shift from less probable, less dispersed arrangements that have fewer ways to arrange the particles to more probable, more dispersed states that have more ways to arrange the particles.
Solids shift spontaneously to gases.

- Why does dry ice, \( \text{CO}_2(s) \), spontaneously shift to \( \text{CO}_2(g) \)?
  - Internal kinetic energy is associated with the random movement of particles in a system.
  - Internal kinetic energy makes it possible for \( \text{CO}_2 \) molecules to move back and forth between solid and gas.
  - If the particles can move freely back and forth between solid and gas, they are more likely to be found in the more dispersed gas state, which has more equivalent ways to arrange the particles.
Solid to Gases

\[ \text{CO}_2(s) \rightarrow \text{CO}_2(g) \]

- Less dispersed \rightarrow More dispersed
- Fewer ways to arrange particles \rightarrow More ways to arrange particles
- Less probable \rightarrow More probable
Gases Expand to Fill Container

When the barrier between the two chambers in the container shown in (a) is raised, it is possible that the gas will end up in one chamber, like in (b), but it is much more likely that it will expand to fill the total volume available to it, like in (c).
Particles tend to disperse (spread out).

<table>
<thead>
<tr>
<th>Gas in one chamber</th>
<th>Gas in both chambers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fewer ways to arrange particles</td>
<td>More ways to arrange particles</td>
</tr>
<tr>
<td>Less probable</td>
<td>More probable</td>
</tr>
<tr>
<td>Less dispersed</td>
<td>More dispersed</td>
</tr>
</tbody>
</table>
Substances tend to mix.

When the barrier between the two gases in the container shown in (a) is raised, it is possible that the gases will stay separated, like in (b), but it is much more likely that they will mix, like in (c).
Ethanol and Water Mixing

At the instant ethanol and water are mixed, the ethanol floats on top of the water.

Because the attractions between their molecules are similar, the molecules mix freely, allowing each substance to disperse into the other.

Hydrogen bonds between ethanol molecules.

Hydrogen bonds between water molecules.

Ethanol and water mix.
Attractions Broken and Made

Hydrogen bond broken

Hydrogen bond broken

Hydrogen bond formed

Hydrogen bond formed
If less than one gram of the substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered **insoluble**.

If more than ten grams of substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered **soluble**.

If between one and ten grams of a substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered **moderately soluble**.
“Like Dissolves Like”

• Polar substances are expected to dissolve in polar solvents.
  – For example, ionic compounds, which are very polar, are often soluble in the polar solvent water.

• Nonpolar substances are expected to dissolve in nonpolar solvents.
  – For example, nonpolar molecular substances are expected to dissolve in hexane, a common nonpolar solvent.
“Like Does Not Dissolve Unlike”

• Nonpolar substances are not expected to dissolve to a significant degree in polar solvents.
  – For example, nonpolar molecular substances are expected to be insoluble in water.

• Polar substances are not expected to dissolve to a significant degree in nonpolar solvents.
  – For example, ionic compounds are insoluble in hexane.
Summary of Solubility Guidelines

• Ionic Compounds
  – Often soluble in water
  – Insoluble in hexane

• Molecular compounds with nonpolar molecules, such as hydrocarbons, \( \text{C}_a\text{H}_b \),
  – Insoluble in water
  – Soluble in hexane

• Molecular Compounds with small polar molecules
  – Usually soluble in water
  – Often soluble in hexane
• We call polar molecules or polar sections of molecules *hydrophilic*.

• We call nonpolar molecules or nonpolar sections of molecules *hydrophobic*.

• If we are comparing the water solubility of two similar molecules, the one with the higher percentage of the molecule that is polar (*hydrophilic*) is expected to have higher water solubility.

• We predict that the molecule with the higher percentage of its structure that is nonpolar (*hydrophobic*) to be less soluble in water.
Hydrophobic and Hydrophilic

amphetamine

epinephrine
Methamphetamine

Nonpolar

CH$_3$NH

Slightly polar

methamphetamine

Nonpolar

CH$_2$NH$_2$$^+$$\text{Cl}^-$

Very polar

methamphetamine hydrochloride
• Soap is made from natural triglycerides, which can be either animal fats or vegetable oils.
• Detergents are made from a variety of chemicals most of which are ultimately derived from petroleum. There is a much greater variety in the structures of detergents.
Triglycerides
(Fats and Oils)

\[
\begin{align*}
H & - C - O - C - R_1 \\
H - C & - O - C - R_2 \\
H - C & - O - C - R_3 \\
H & \\
\end{align*}
\]

triglyceride

Hydrocarbon groups
Tristearin
Tristearin – Line Drawing
Typical Liquid Triglyceride
Making Soap

Triglyceride in fat or oil

\[3 \text{NaOH} \downarrow\]

glycerol

\[\text{soap}\]
Soap and Detergent

Typical soap

SDS, a typical ionic detergent
Cleaning Greasy Dishes

Without soap or detergent, droplets recombine.

Soap or detergent anions keep droplets suspended.

Oil

Agitation

Oil breaks into droplets.
Oil Droplets and Soap or Detergent

Hydrophobic ends of soap or detergent enter droplet.

Hydrophilic ends of soap or detergent stick out into the water.

Coated with negative charges, droplets repel each other.
Questions to Answer

• What’s happening at the molecular level as a solid dissolves in a liquid?
• Why is there a limit to the amount of solid that will dissolve in a given amount of solvent?
• What’s going on when a mixture reaches the solubility limit?
• Why does powdered solid dissolve faster than solid with larger particles?
• How does agitation or stirring affect the process?
• How does temperature affect the process?
• Do particle size, agitation, or temperature change the solubility limit?
Particles into Solution

1. Molecules moving out into the water
2. Collisions push the molecules farther out into the water.
3. Water molecules move to disrupt the attractions to the solid.
4. Attractions between the water and sugar molecules

Solid sugar added to water
Particles Return to Solid

Some particles are moving into solution

Some particles are returning to the solid

Solid sugar added to water
Dynamic Equilibrium in a Saturated Solution

Rate of return equals rate of solution

No net change in the amount of solid or dissolved solute
Dynamic Equilibrium and Saturated Solutions

Addition of a large amount of solid to a liquid

- Initially, rate of solution is greater than the rate of return
- Net increase in number and concentration of particles in solution
- Increased rate of collision between dissolved particles and solid
- Increased rate of return...
- ...Until rate of return equals rate of solution
- Constant changes from solid to dissolved solute and back, but no net change in amounts of solid and dissolved solute

Saturated solution due to dynamic equilibrium
Saturated and Unsaturated Solutions

• A **saturated solution** is a solution that is at the solubility limit, either because
  – it contains an excess of solid with a dynamic equilibrium between the rate of solution and the rate of return
  – or it has reached the dynamic equilibrium and the excess solid has been filtered out.

• An **unsaturated solution** is a solution that has less solute than the solubility limit, either because
  – all the solid dissolves before the dynamic equilibrium is reached
  – or there just has not been enough time for the dynamic equilibrium to be reached.
Rate of Solution
Dependent on:

- Surface area of the solute
- Degree of agitation or stirring
- Temperature
Surface Area and Rate of Solution

The rate of solution depends on the number of particles at the solid’s surface.

If the solid is fragmented, new surfaces are exposed, allowing more particles to escape into solution.
Agitation and Rate of Solution

Without stirring:
- More particles near the solid leads to a higher rate of return.
- Lower net rate of solution.

With stirring:
- Fewer particles near the solid leads to a lower rate of return.
- Higher net rate of solution.
Agitation and Rate of Solution

Increased agitation

↓

Decreased concentration of dissolved solute particles near the solid

↓

Decreased rate of return to the solid

↓

Increased difference between the rate of solution and the rate of return

↓

Increased net rate of solution
Temperature and Rate of Solution

Increased temperature

$\downarrow$

Increased velocity of particles

$\downarrow$

Particles in solution move away from the solid more rapidly

$\downarrow$

Increased net rate of solution
Temperature and Increased Solubility Limit

Increased temperature

\[ \text{Increased} \Rightarrow \text{Increased velocity and momentum of particles} \]

\[ \text{Increased} \Rightarrow \text{Easier for particles to escape attractions and move into solution} \]

\[ \text{Increased} \Rightarrow \text{Increased rate of solution} \]

\[ \text{Increased} \Rightarrow \text{Increased rate of return necessary to be equal to the increased rate of solution} \]

\[ \text{Increased} \Rightarrow \text{Increased concentration necessary to yield the increased rate of return} \]

Increased solubility limit
Questions to Answer

• Why does increased carbon dioxide in the atmosphere due to burning fossil fuels and deforestation lead to increased CO$_2$ dissolved in the ocean?
• Why does this cause the ocean to become more acidic?
• How does the increasing acidity of the ocean affect sea organisms?
• Why should this worry us?
Solution of Gas in Liquid
Gas Solubility

Add a gas above a liquid in a closed container

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

Increased rate of escape...

...Until the rate of escape equals rate of solution

Dynamic equilibrium (solubility limit)

Increased concentration of dissolved gas

Constant changes between dissolved and undissolved gas, but no net change in amount of either
Dynamic Equilibrium for Gas Dissolved in Liquid

The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.
Partial Pressure and Gas Solubility

Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)

- Increased rate of collision between gas particles and liquid → Increased rate of solution
- Net movement of gas particles into solution ← Rate of solution greater than rate of escape
- Increased concentration of solute in solution → Increased rate of escape until it equals the higher rate of solution

Greater solubility
One way that carbon enters the ocean is through solution of atmospheric CO$_2$.

\[
\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq)
\]

Increased concentration of CO$_2$ in the atmosphere due to the burning of fossil fuels and deforestation leads to

- an increase in the rate of collisions with the ocean,
- increasing the rate of solution,
- disrupting the dynamic equilibrium, making the \( R_{\text{soln}} > R_{\text{escape}} \),
- and leading to a net shift of CO$_2$ into the ocean.
• CO₂ molecules react with water to form carbonic acid.

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \]

• Carbonic acid reacts with water to form hydronium and hydrogen carbonate ions.

\[ \text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \]
The absorption of human generated CO$_2$ has acidified the surface layers of the ocean, with a steady decrease of about 0.02 pH units per decade over the past 30 years and an overall decrease since the pre-industrial period of 0.1 pH units.

Because the pH scale is a logarithmic scale, this is a 30% increase in hydronium ion concentration.

This leads to substantial changes in ocean chemistry.
Effects of Increasing Ocean Acidity

• Carbonate ions combine with calcium ions in the ocean to form calcium carbonate, which forms shells, skeletons for coral reefs and other sea animals, and other CaCO$_3$ structures of ocean organisms.

\[
\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s})
\]

• Hydronium ions react with carbonate ions to form hydrogen carbonate ions, decreasing the carbonate ions available to build and maintain calcium carbonate structures.

\[
\text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]
Effects of Increasing Ocean Acidity

- Ocean acidification affects organisms in other ways than decreasing carbonate ions. For example,
  - seagrasses may grow faster if more dissolved carbon dioxide is available,
  - the number of oysters may decrease as fewer larvae complete their life cycle,
  - the ability of some fish, such as clownfish, to detect predators and find suitable habitats decreases in more acidic waters, threatening the whole ocean food web.