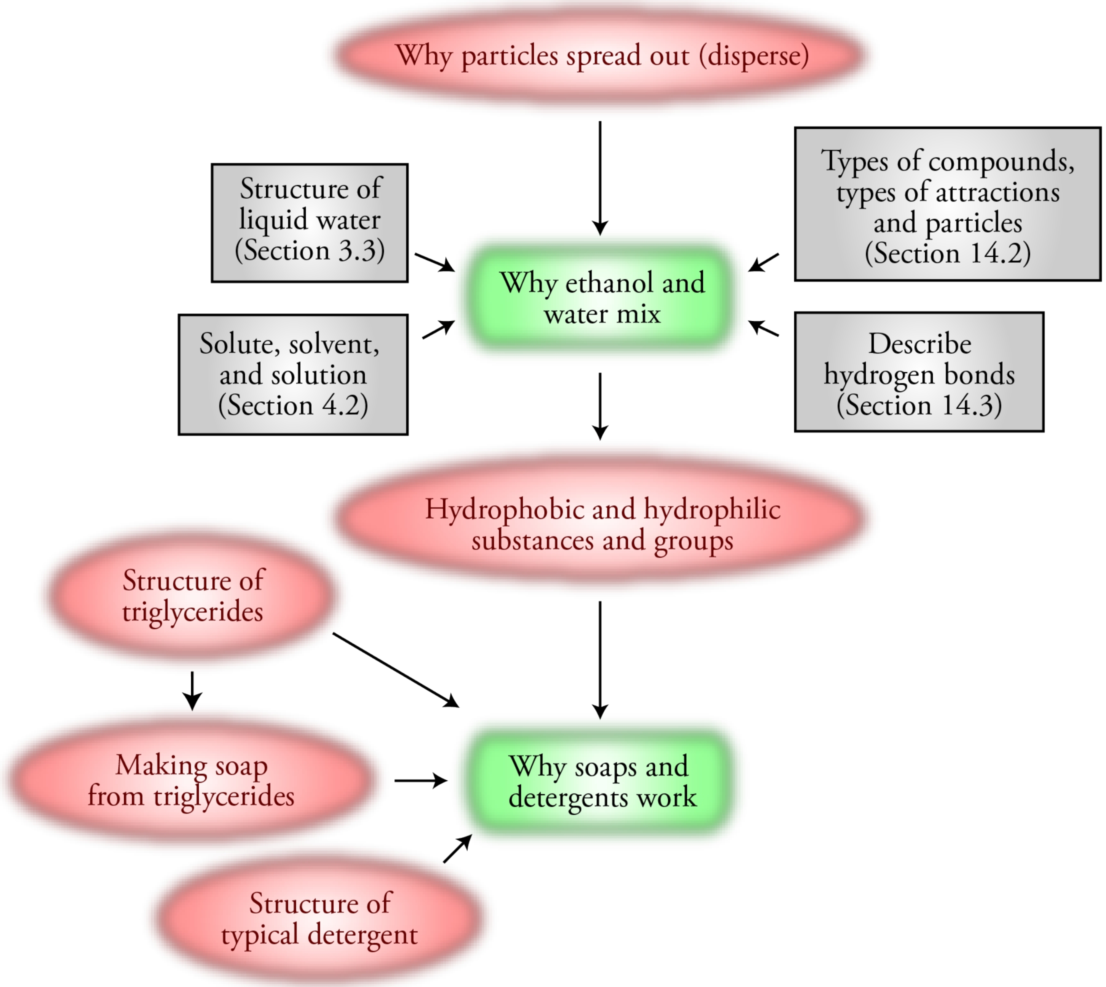
Chapter 15
Solution Dynamics

An Introduction to Chemistry

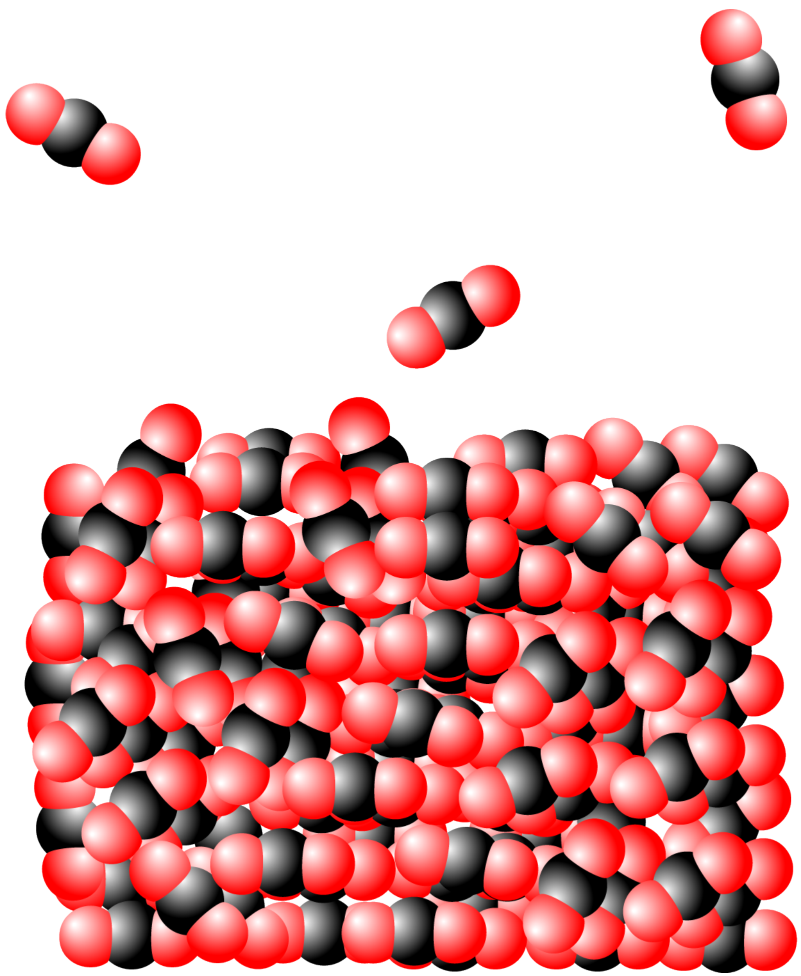
by Mark Bishop

Chapter Map


Why particles spread out (disperse)
Structure of liquid water (Section 3.3)
Types of compounds, types of attractions and particles (Section 14.2)
Why ethanol and water mix
Solute, solvent, and solution (Section 4.2)
Describe hydrogen bonds (Section 14.3)
Hydrophobic and hydrophilic substances and groups
Structure of triglycerides
Making soap from triglycerides
Why soaps and detergents work
Structure of typical detergent

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.

State A		State B
$CO_2(s)$	$\rightleftharpoons$ $\rightleftharpoons$	$CO_2(g)$
Less dispersed (spread out)		More dispersed (spread out)
Fewer ways to arrange particles and energy		More ways to arrange particles and energy
Less probable		More probable

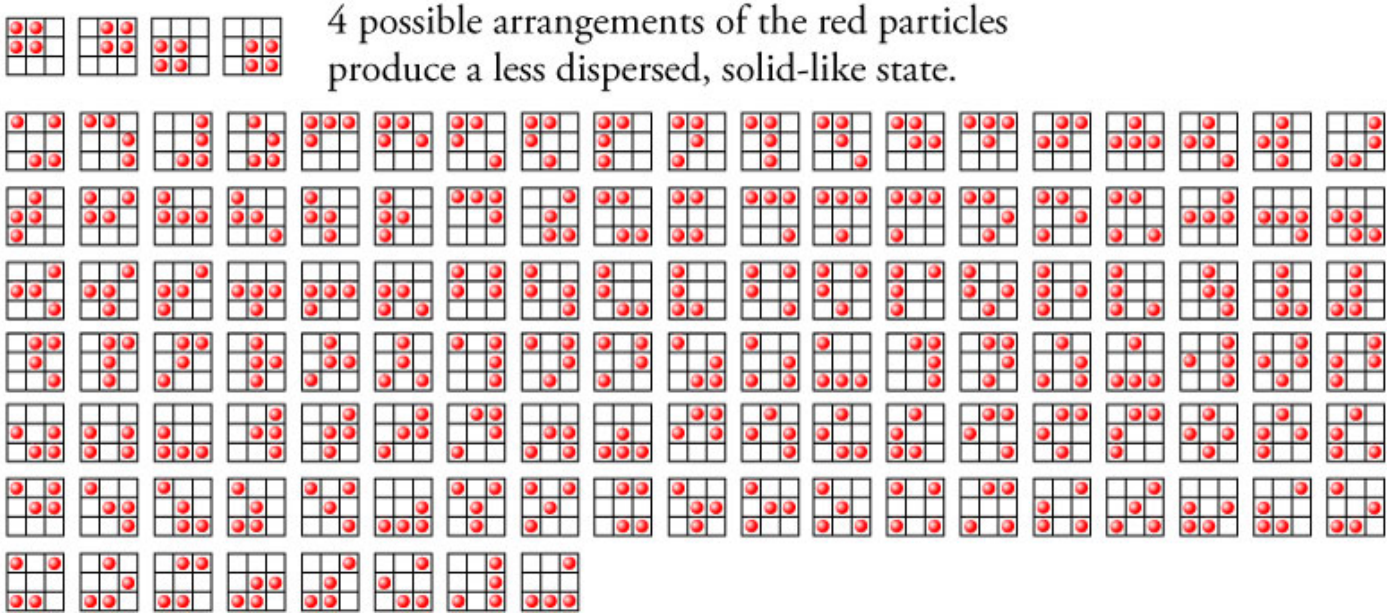
9-Point Universe

Solid-like states

4 possible arrangements of the red particles produce a less dispersed, solid-like state.

Gas-like states

122 possible arrangements produce a more dispersed, gas-like state.



Probability of Gas

- 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.

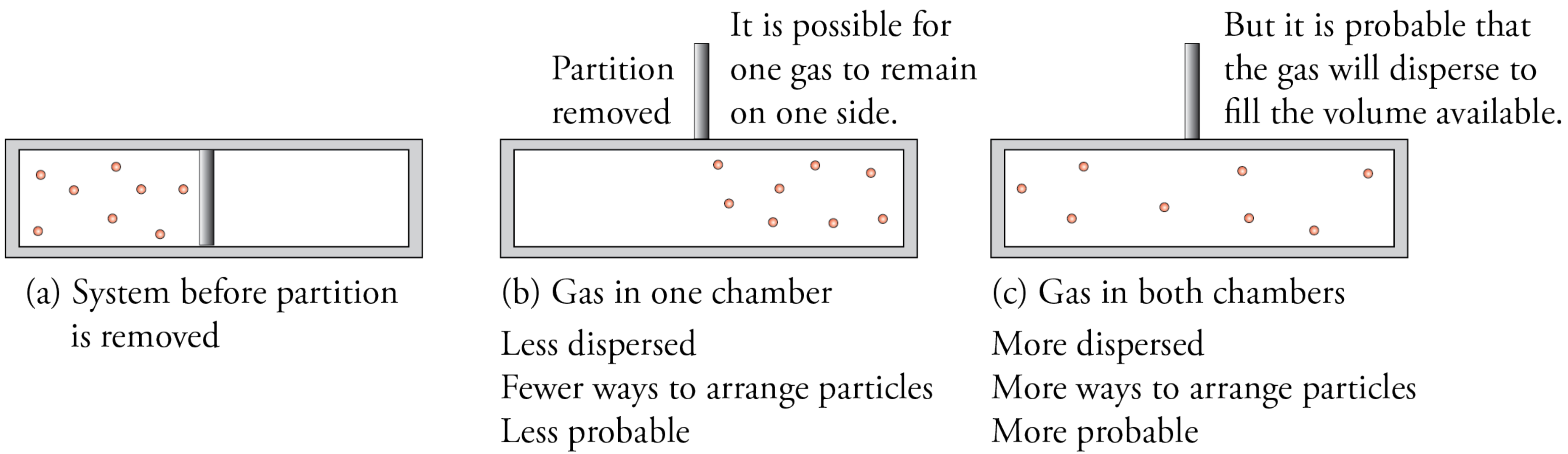
- Why does dry ice, $CO_2(s)$, spontaneously shift to $CO_2(g)$?
  - Internal kinetic energy is associated with the random movement of particles in a system.
  - Internal kinetic energy makes it possible for CO_2 molecules to move back and forth between solid and gas.
  - If the particles can move freely 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

$$CO_2(s) \longrightarrow CO_2(g)$$

Less dispersed	More dispersed
Fewer ways to arrange particles	More ways to arrange particles
Less probable	More probable

Gases Expand to Fill Container

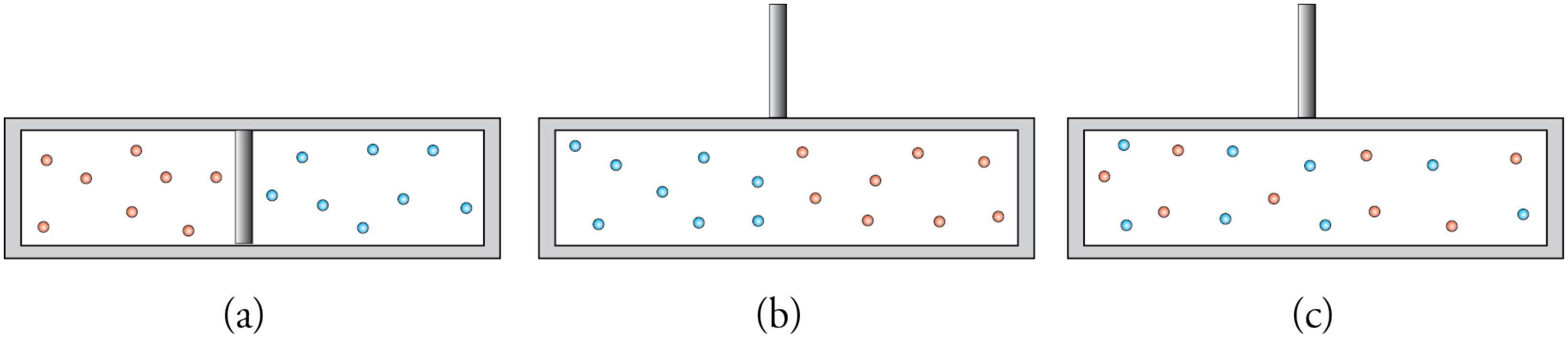


When the barrier between the two chambers in the container shown in (a) is raised, it is possible that the gas will end up in one chamber, like in (b), but it is much more likely that it will expand to fill the total volume available to it, like in (c).

Particles tend to disperse (spread out).

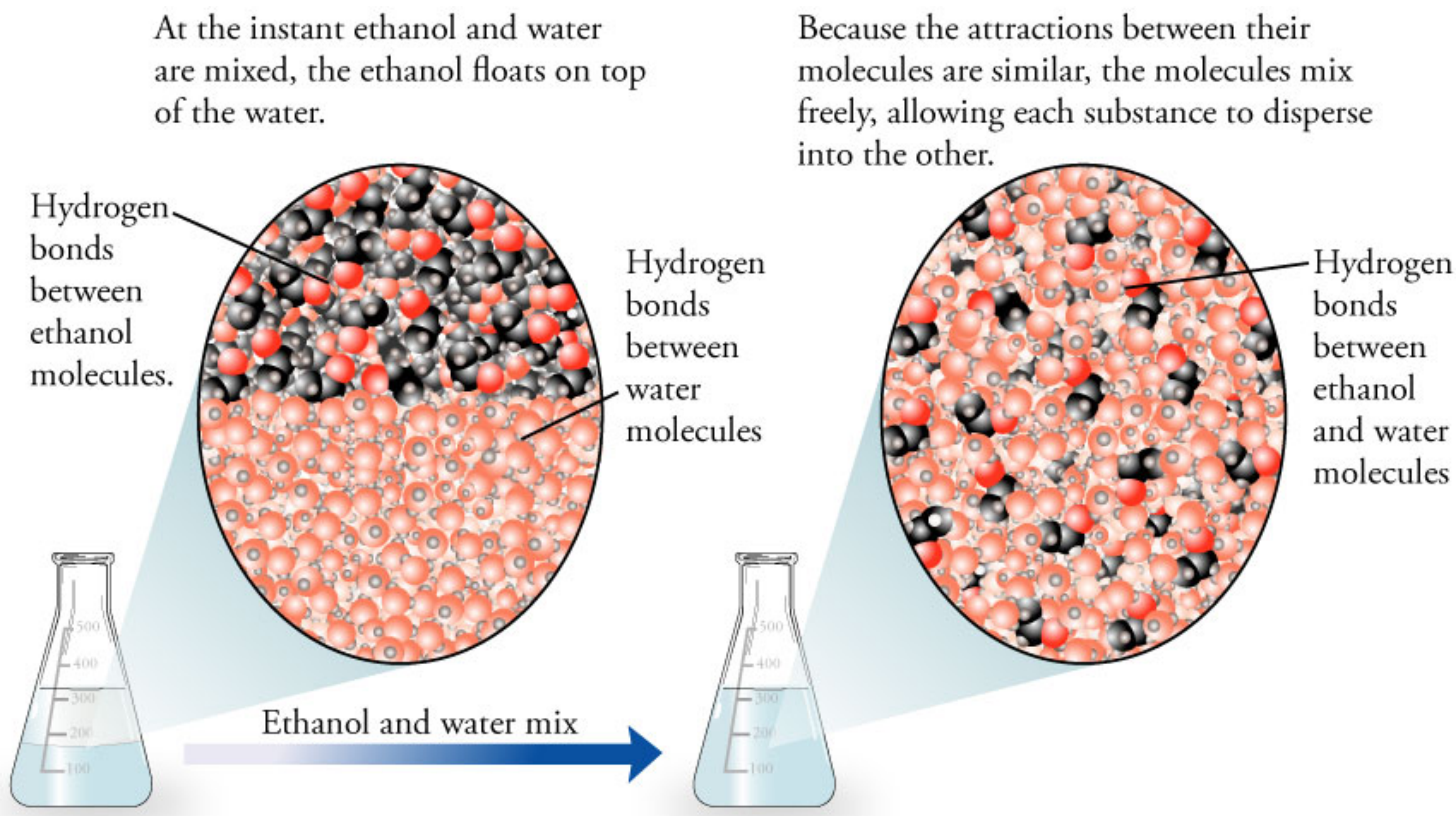
Gas in one chamber	→	Gas in both chambers
Fewer ways to arrange particles		More ways to arrange particles
Less probable		More probable
Less dispersed		More dispersed

Substances tend to mix.

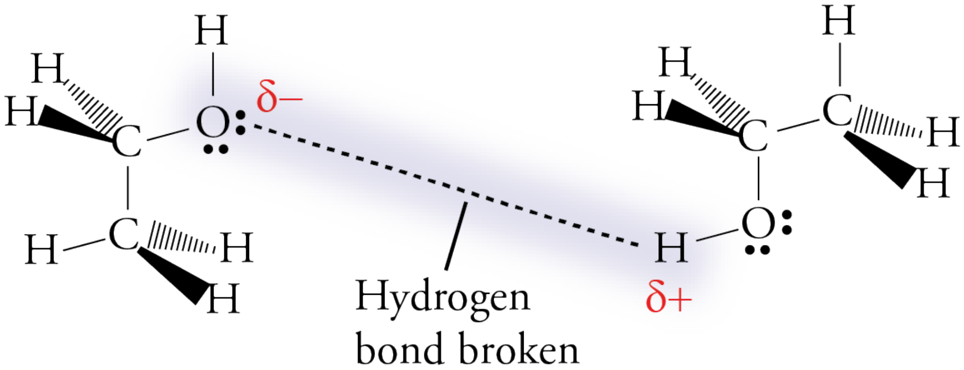


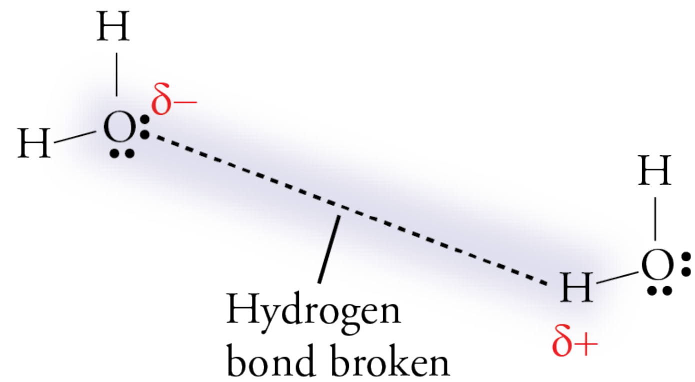
When the barrier between the two gases in the container shown in (a) is raised, it is possible that the gases will stay separated, like in (b), but it is much more likely that they will mix, like in (c).

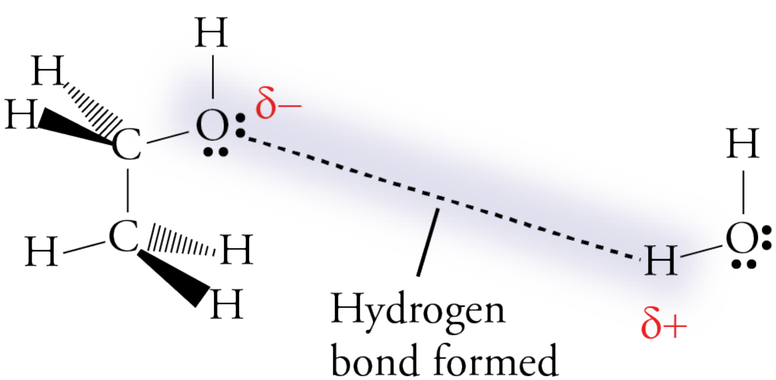
Ethanol and Water Mixing

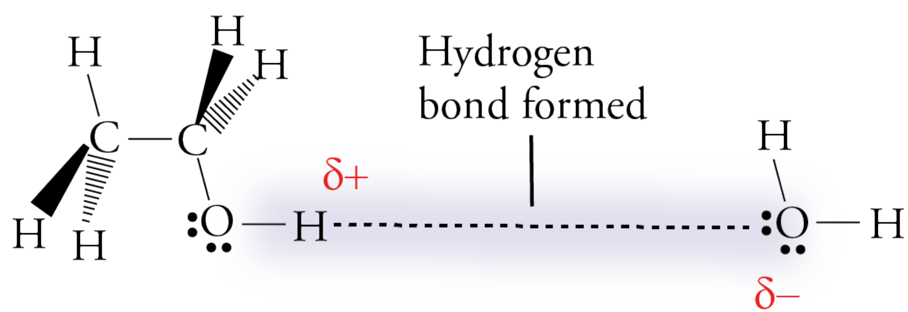


Attractions Broken and Made









Solubility

- 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.

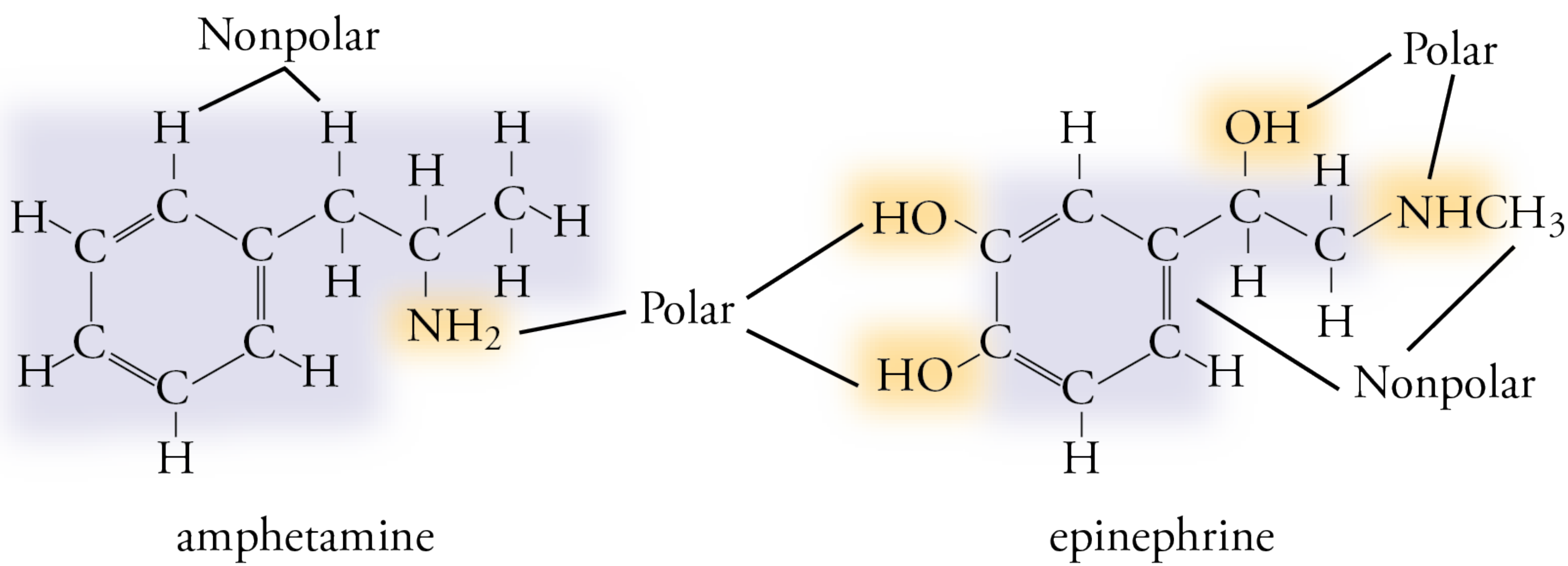
Summary of Solubility Guidelines

- Ionic Compounds
  - Often soluble in water
  - Insoluble in hexane
- Molecular compounds with nonpolar molecules, such as hydrocarbons, C_aH_b,
  - Insoluble in water
  - Soluble in hexane
- Molecular Compounds with small polar molecules
  - Usually soluble in water
  - Often soluble in hexane

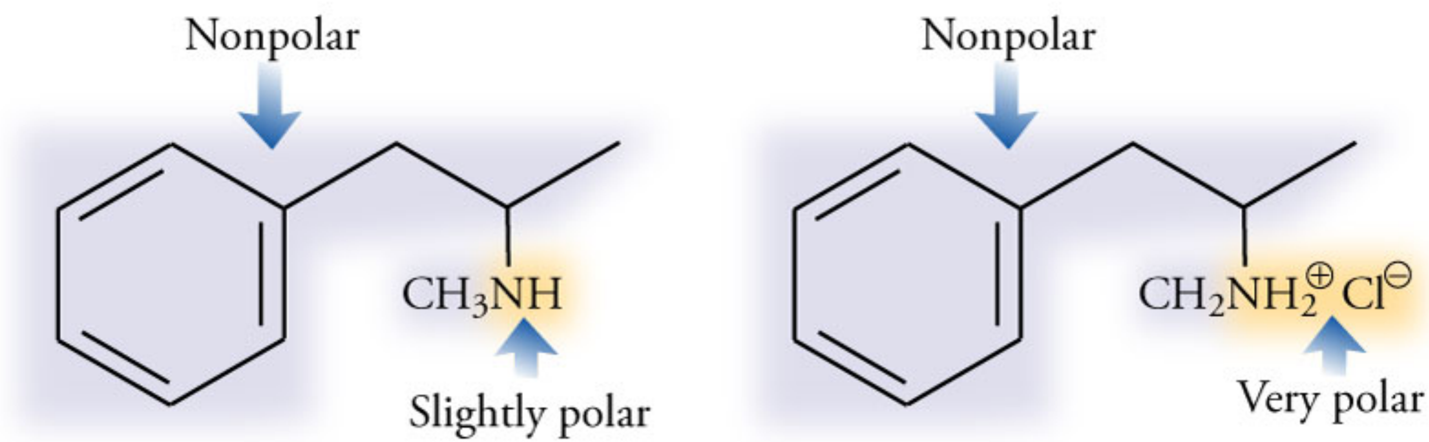
Water Solubility

- 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



Methamphetamine



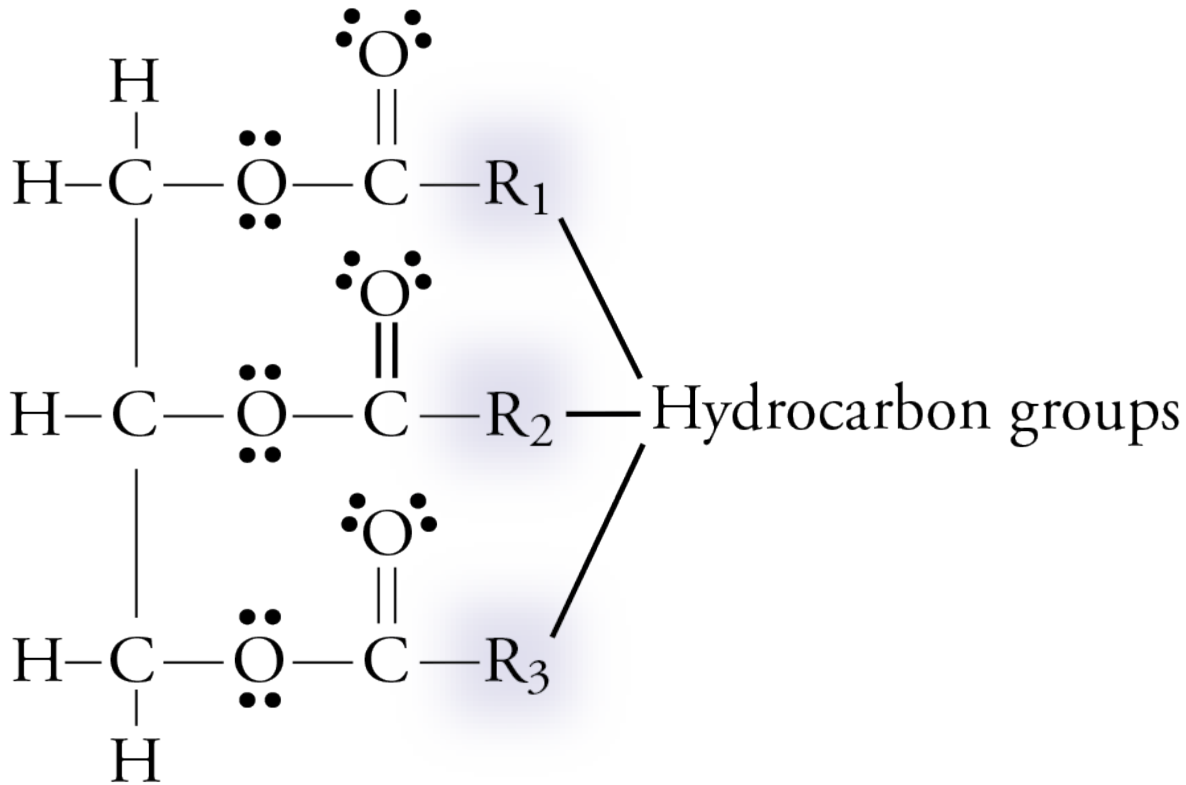
methamphetamine

methamphetamine hydrochloride

Soaps and Detergents

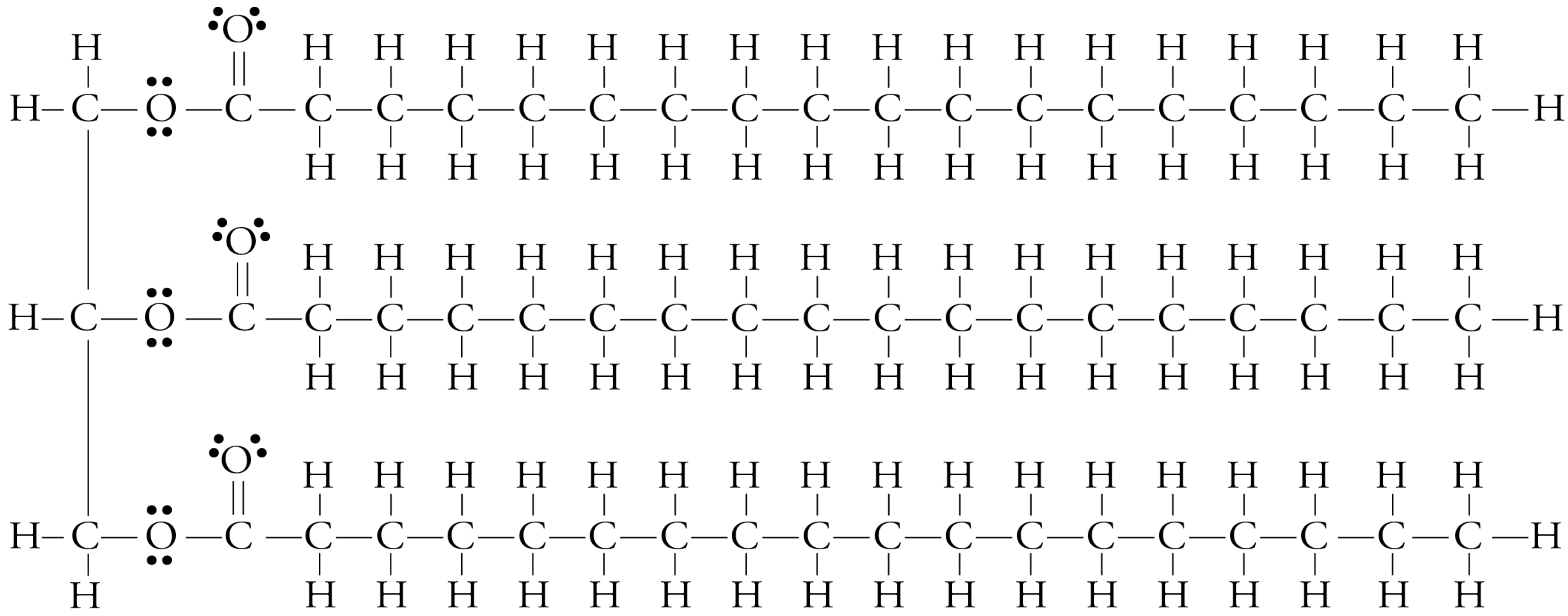
- Soap is made from natural triglycerides, which can be either animal fats or vegetable oils.
- Detergents are made from a variety of chemicals most of which are ultimately derived from petroleum. There is a much greater variety in the structures of detergents.

Triglycerides (Fats and Oils)

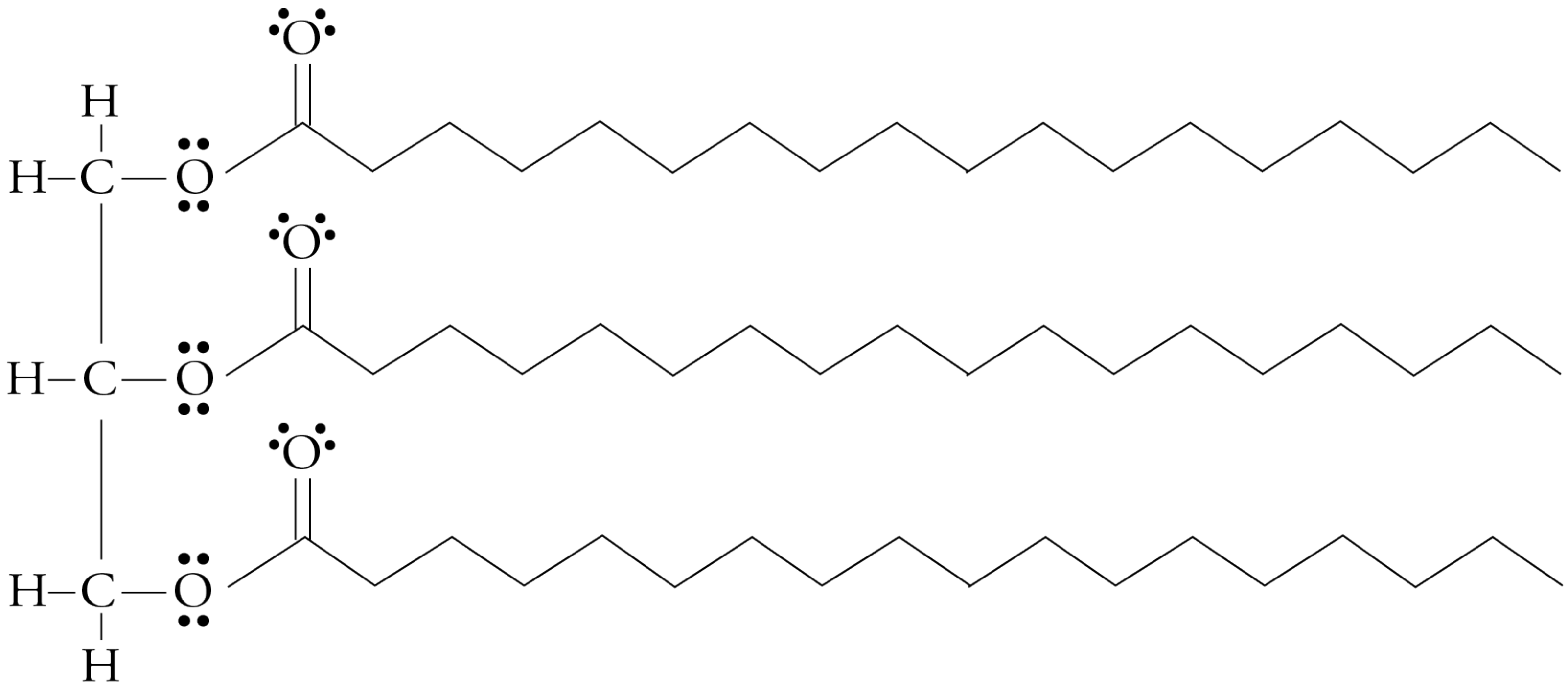


triglyceride

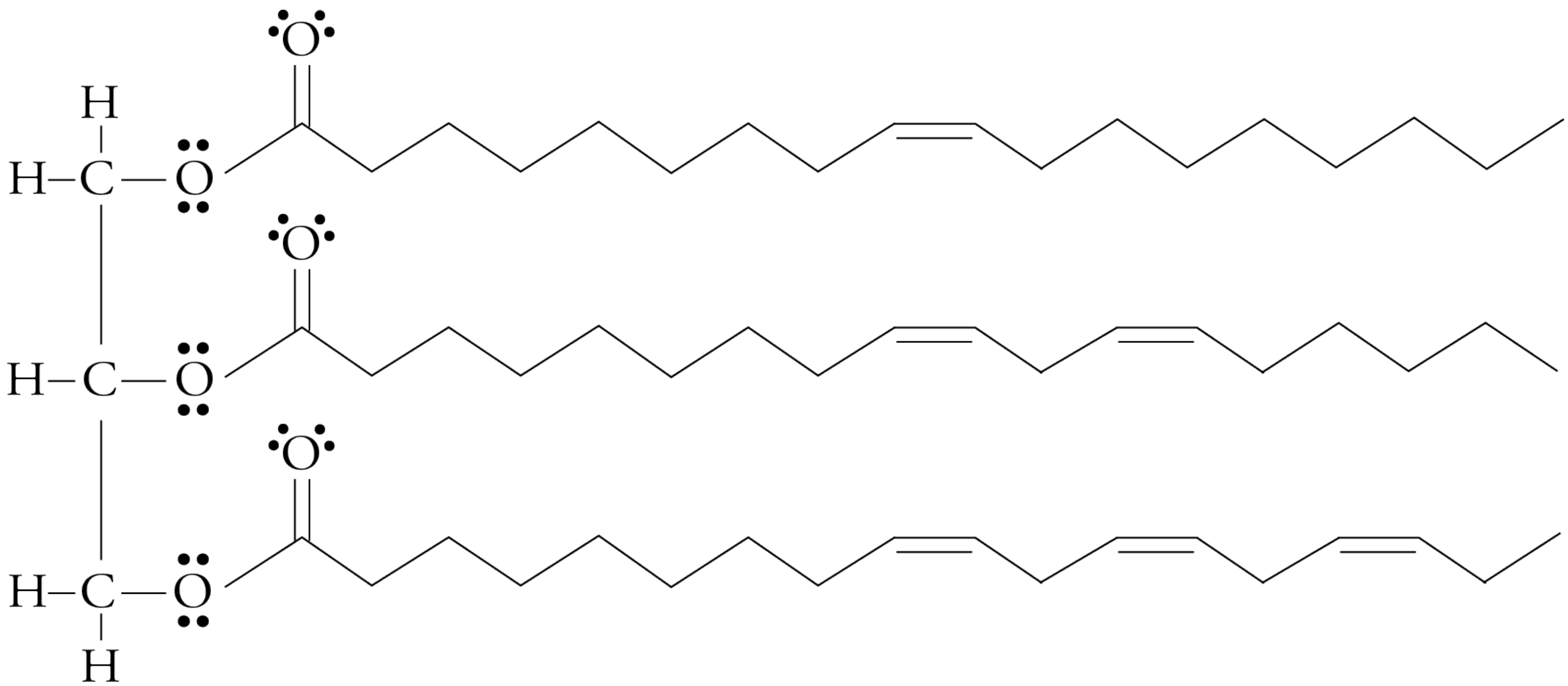
Tristearin



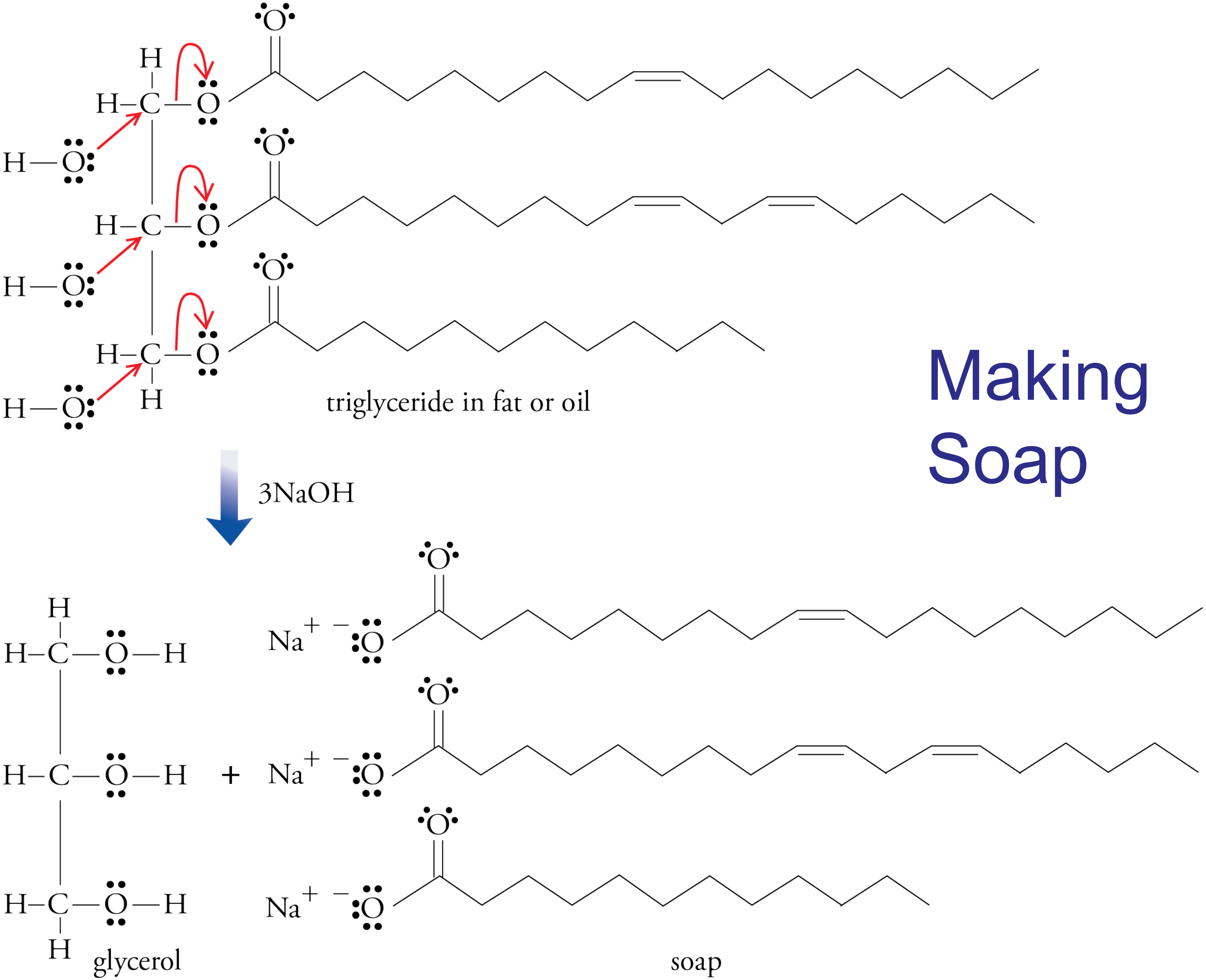
Tristearin – Line Drawing



Typical Liquid Triglyceride

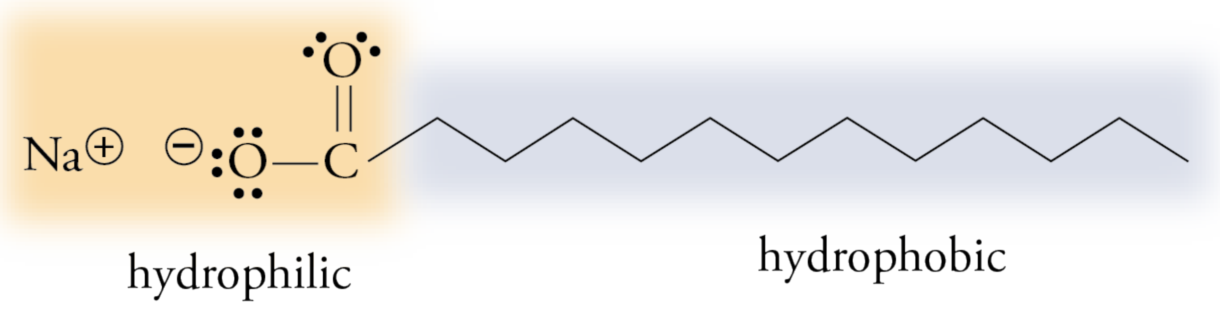


Making Soap

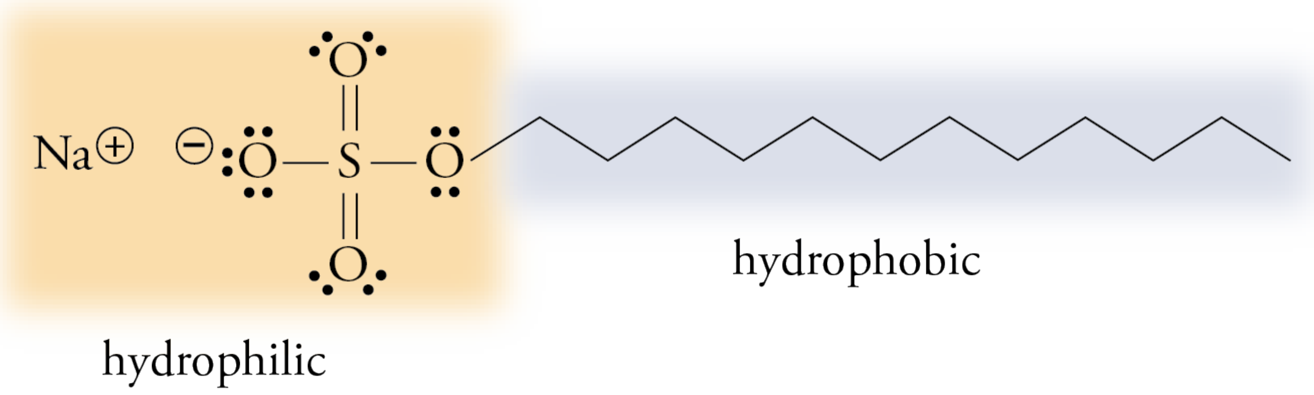


Soap and Detergent

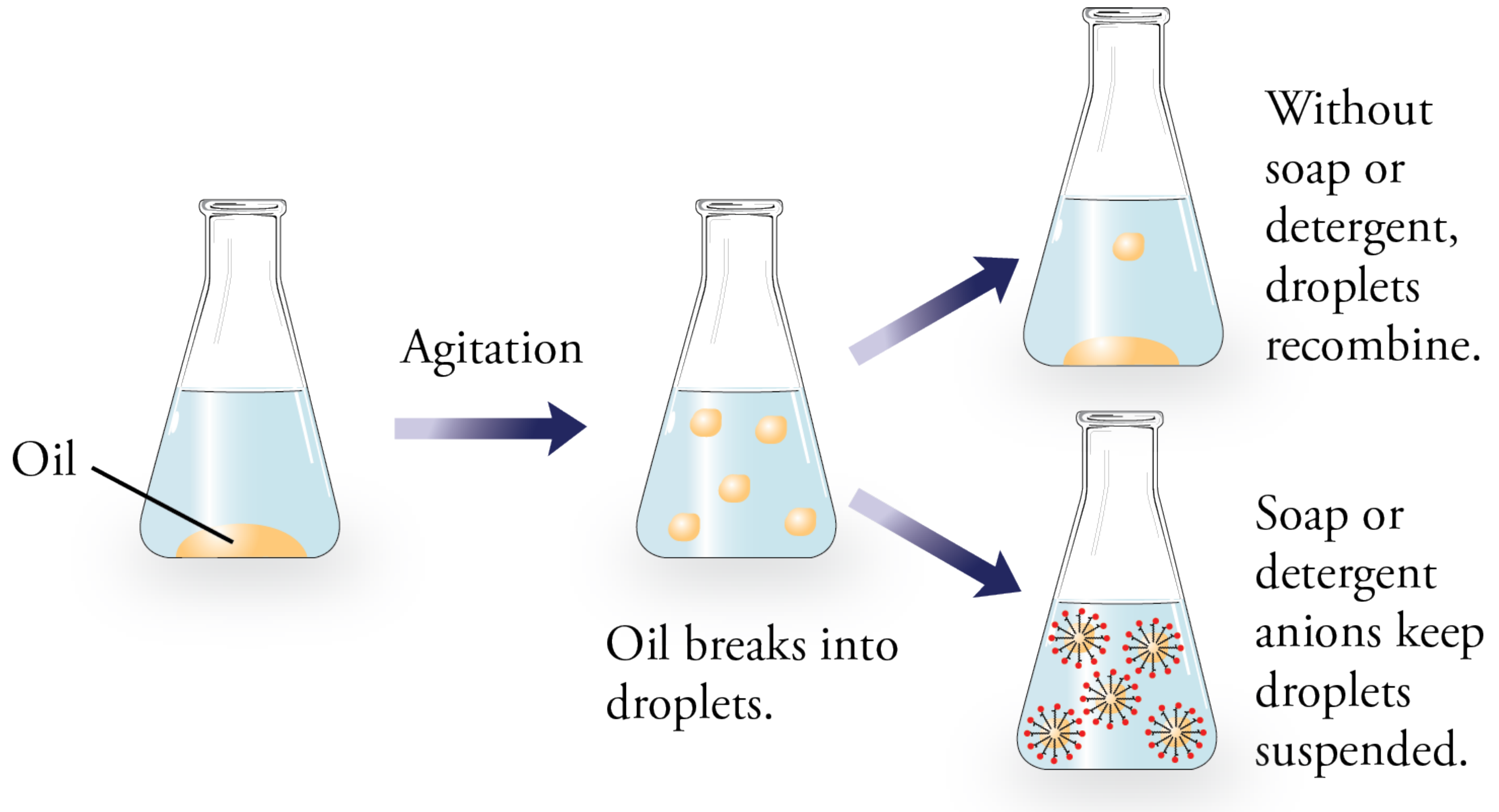
Typical soap



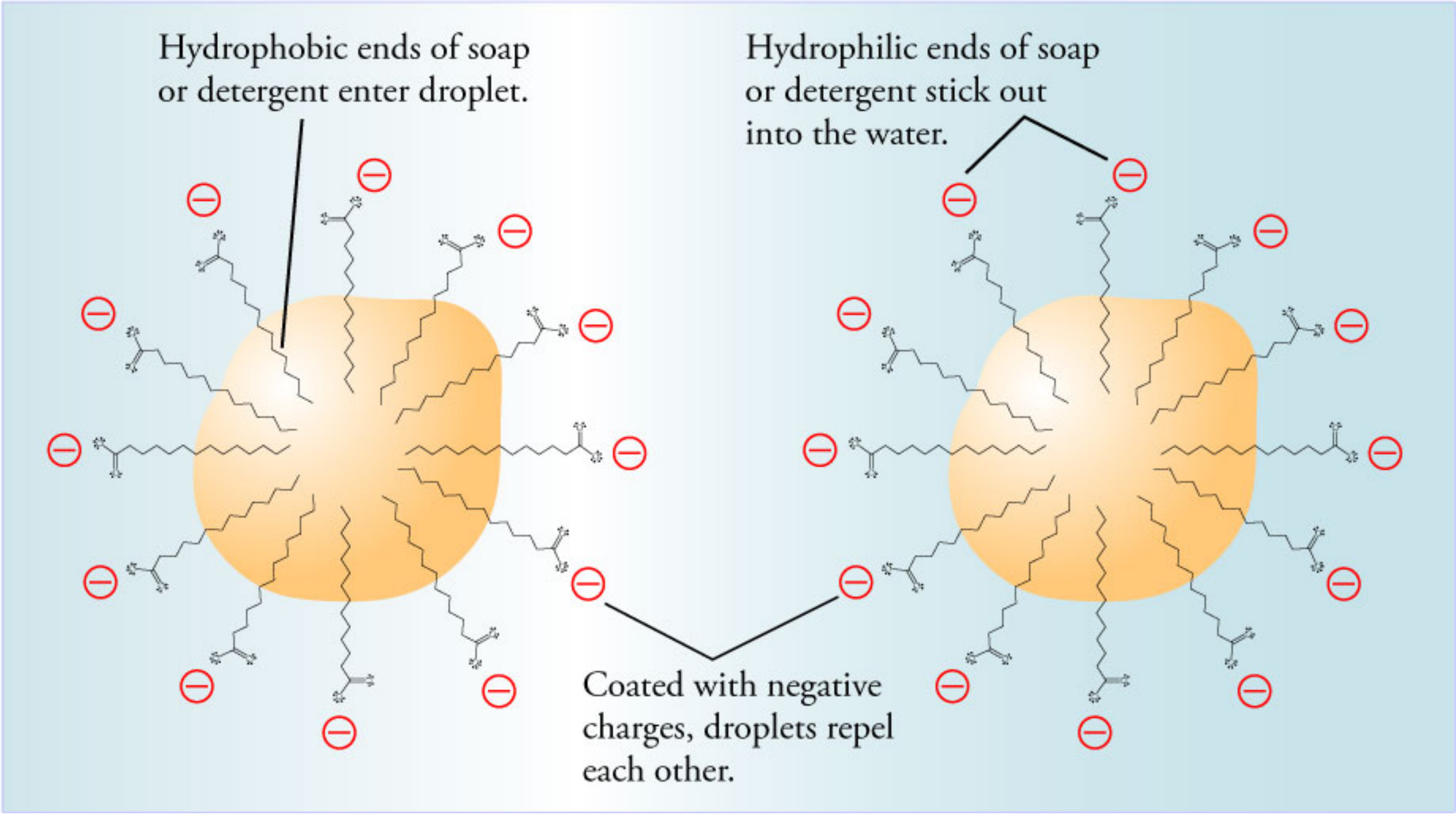
SDS, a typical ionic detergent



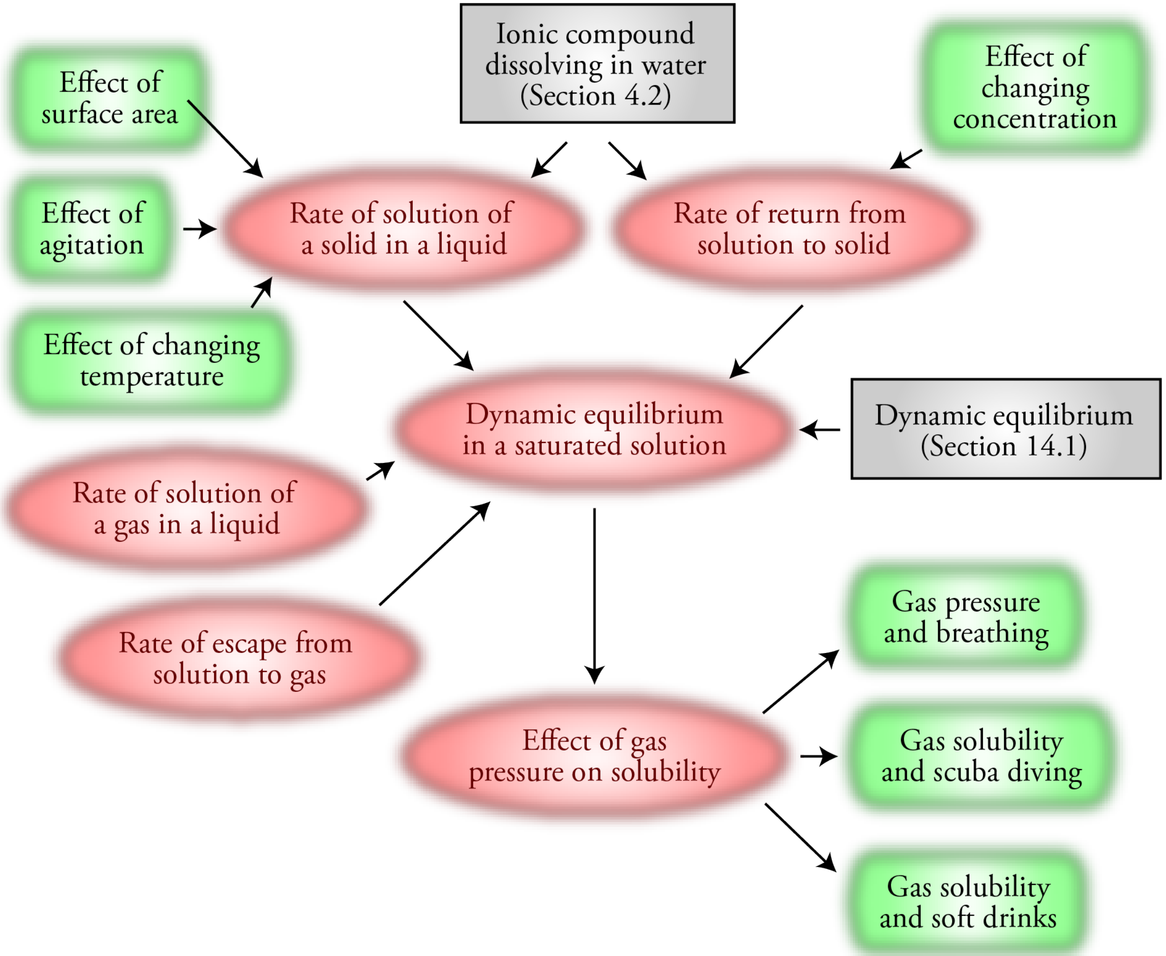
Cleaning Greasy Dishes



Oil Droplets and Soap or Detergent



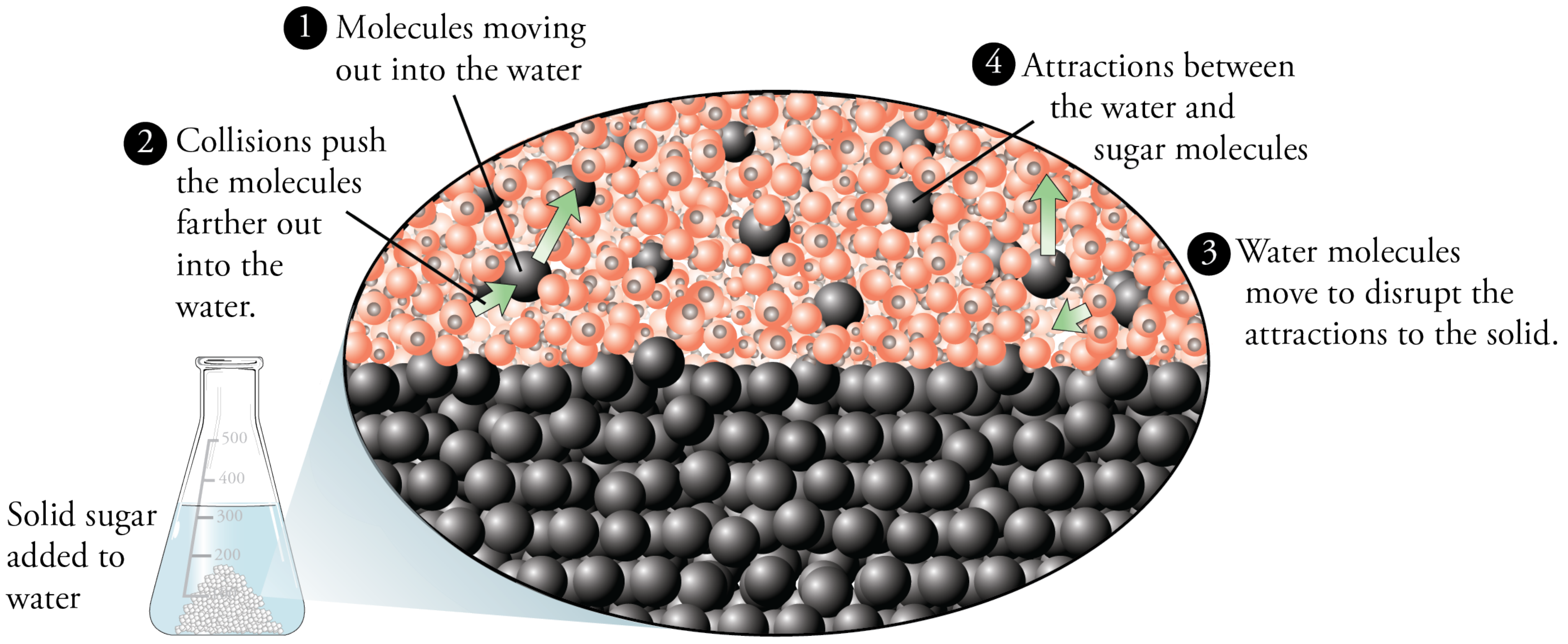
Chapter 15 – part 2



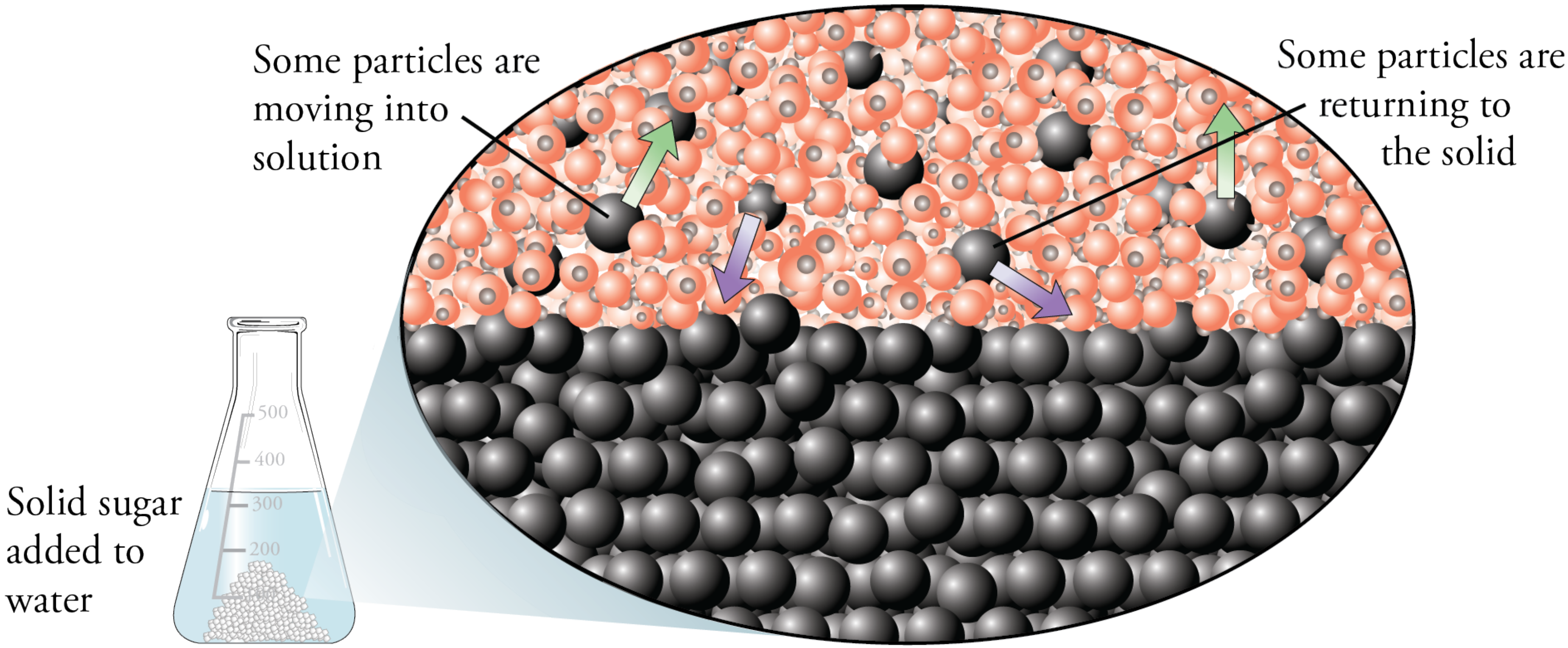
Questions to Answer

- 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?

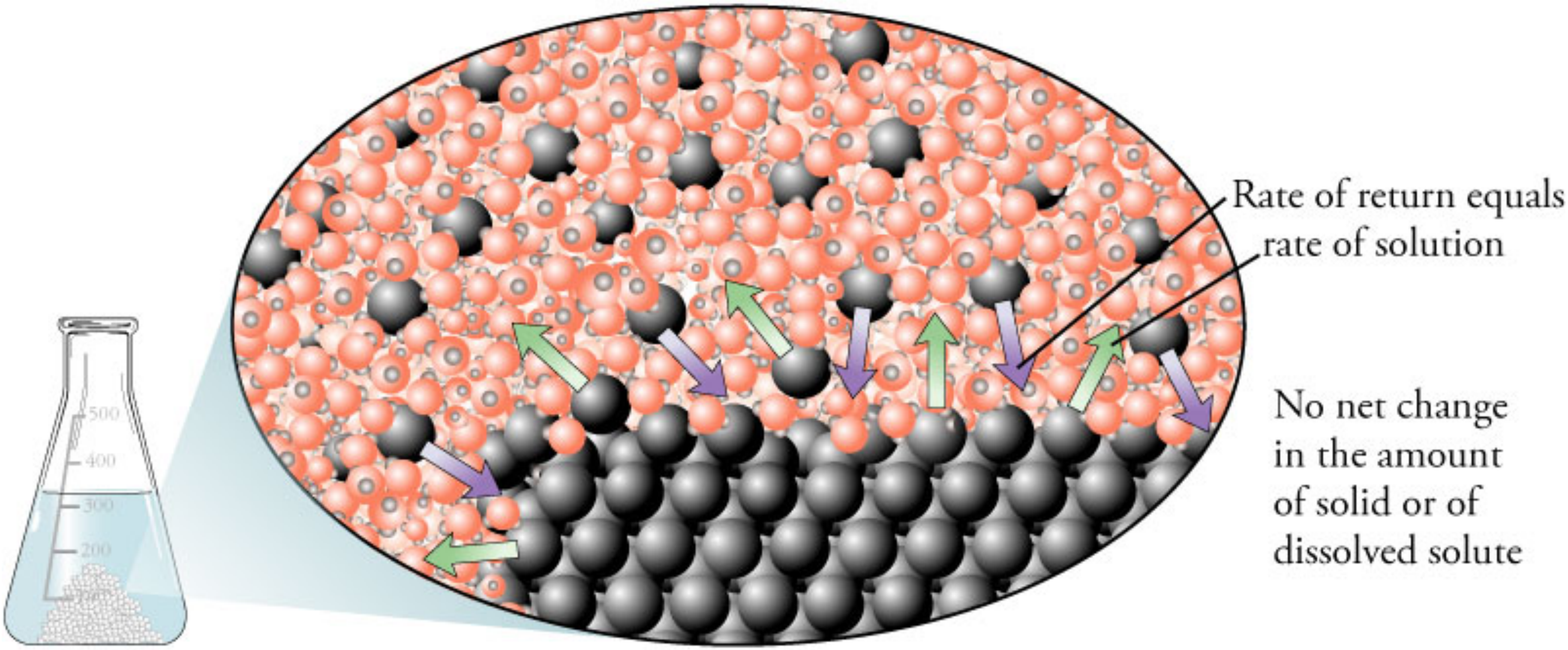
Particles into Solution



Particles Return to Solid



Dynamic Equilibrium in a Saturated Solution



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

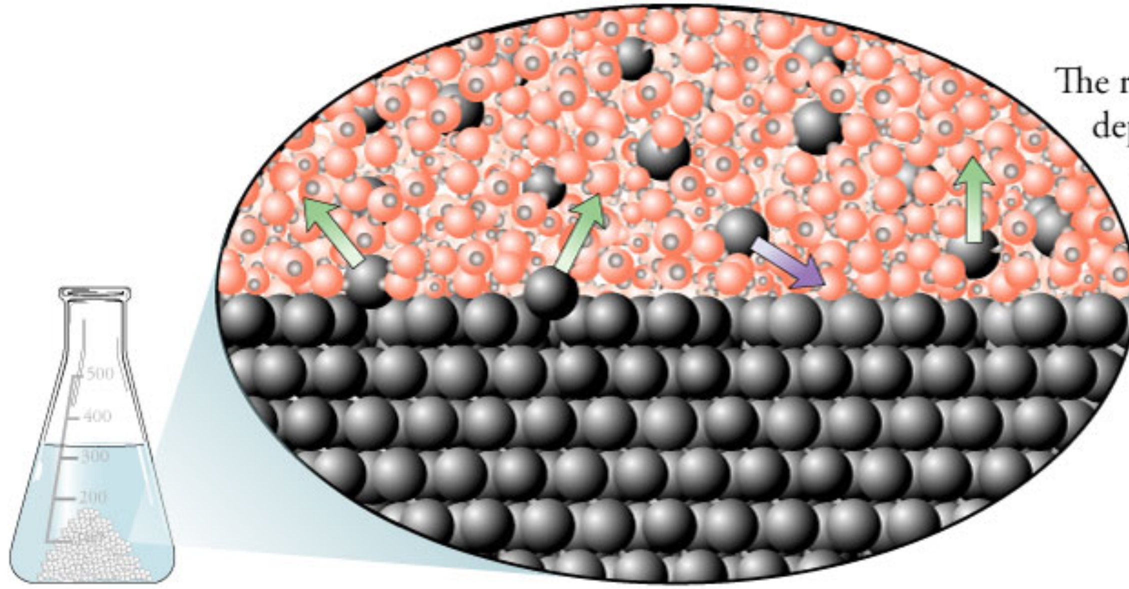
Saturated and Unsaturated Solutions

- 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.

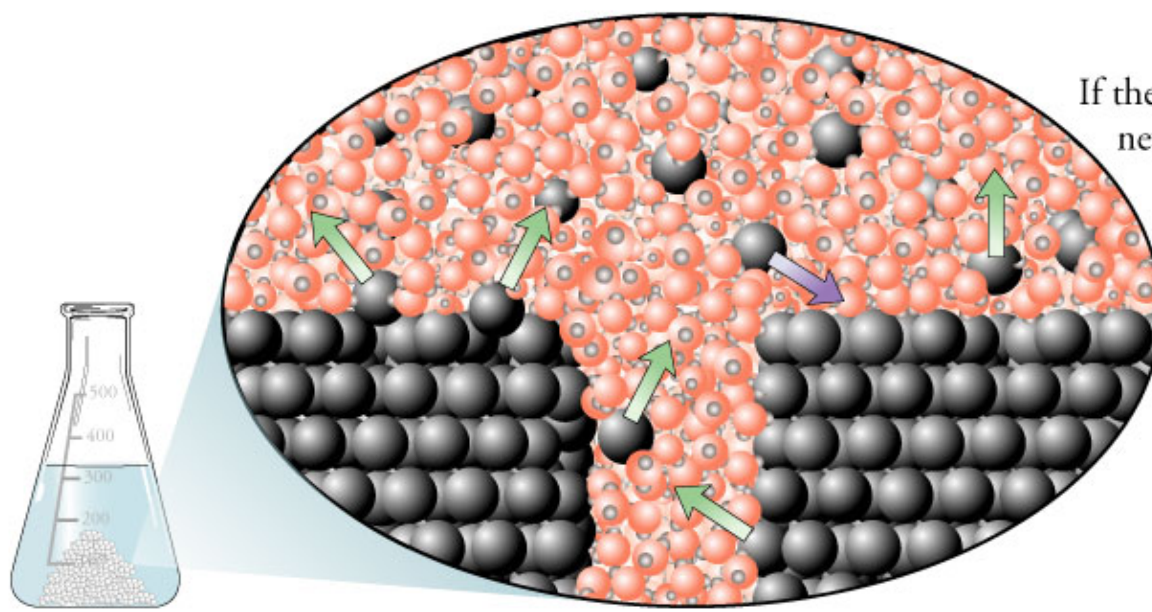
Rate of Solution Dependent on:

- Surface area of the solute
- Degree of agitation or stirring
- Temperature

Surface Area and Rate of Solution

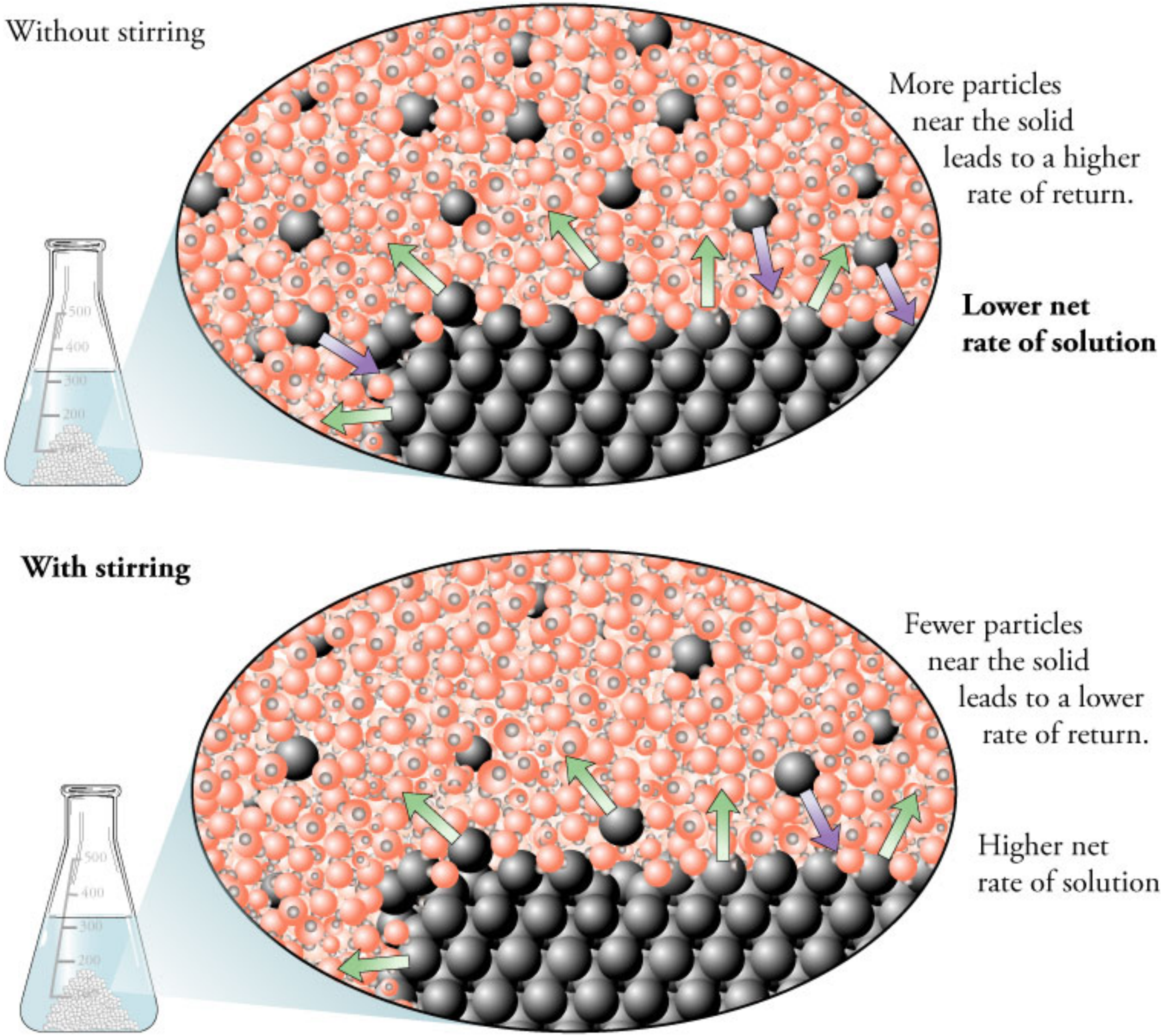


The rate of solution depends on the number of particles at the solid's surface.



If the solid is fragmented, new surfaces are exposed, allowing more particles to escape into solution.

Agitation and Rate of Solution



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

↓

Increased velocity of particles

↓

Particles in solution move away from the solid more rapidly

↓

Increased net rate of solution

Temperature and Increased Solubility Limit

Increased temperature

↓

Increased velocity and momentum of particles

↓

Easier for particles to escape attractions and move into solution

↓

Increased rate of solution

↓

Increased rate of return necessary to be equal to the increased rate of solution

↓

Increased concentration necessary to yield the increased rate of return

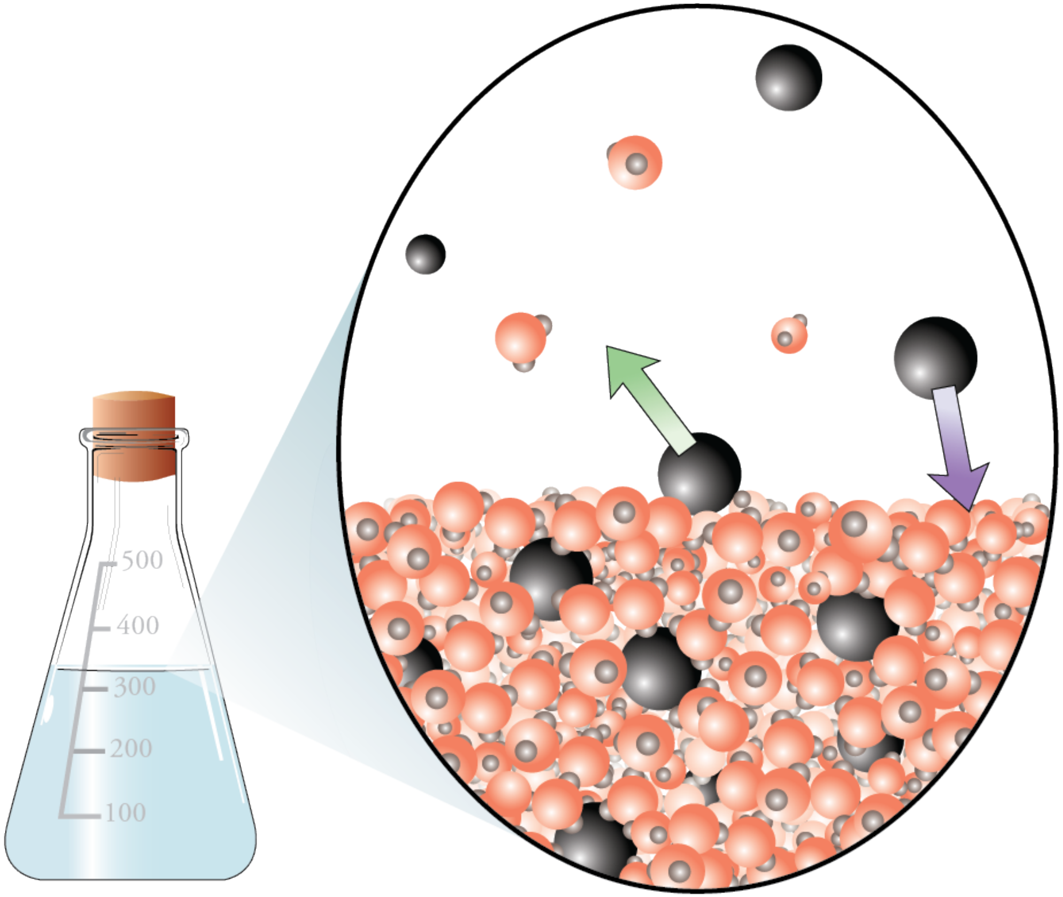
↓

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… ← Increased concentration of dissolved gas

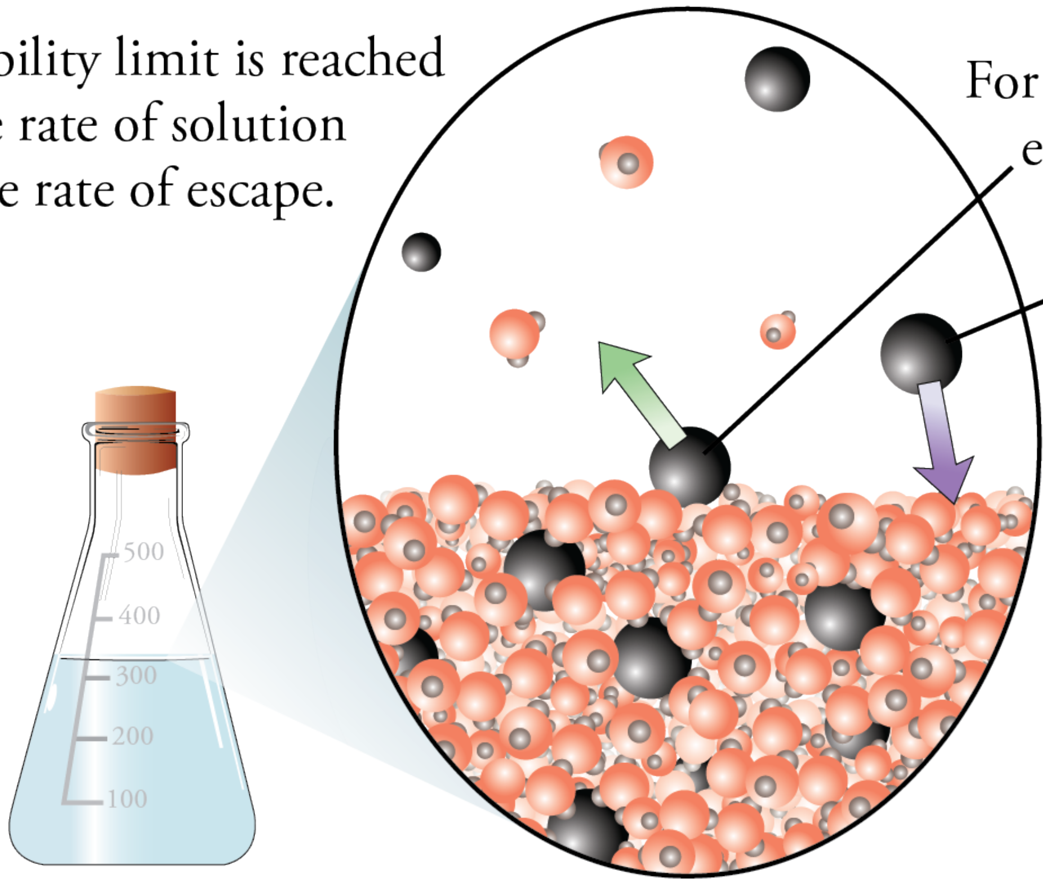
↓

…Until the rate of escape equals rate of solution → Constant changes between dissolved and undissolved gas, but no net change in amount of either

Dynamic equilibrium (solubility limit) ←

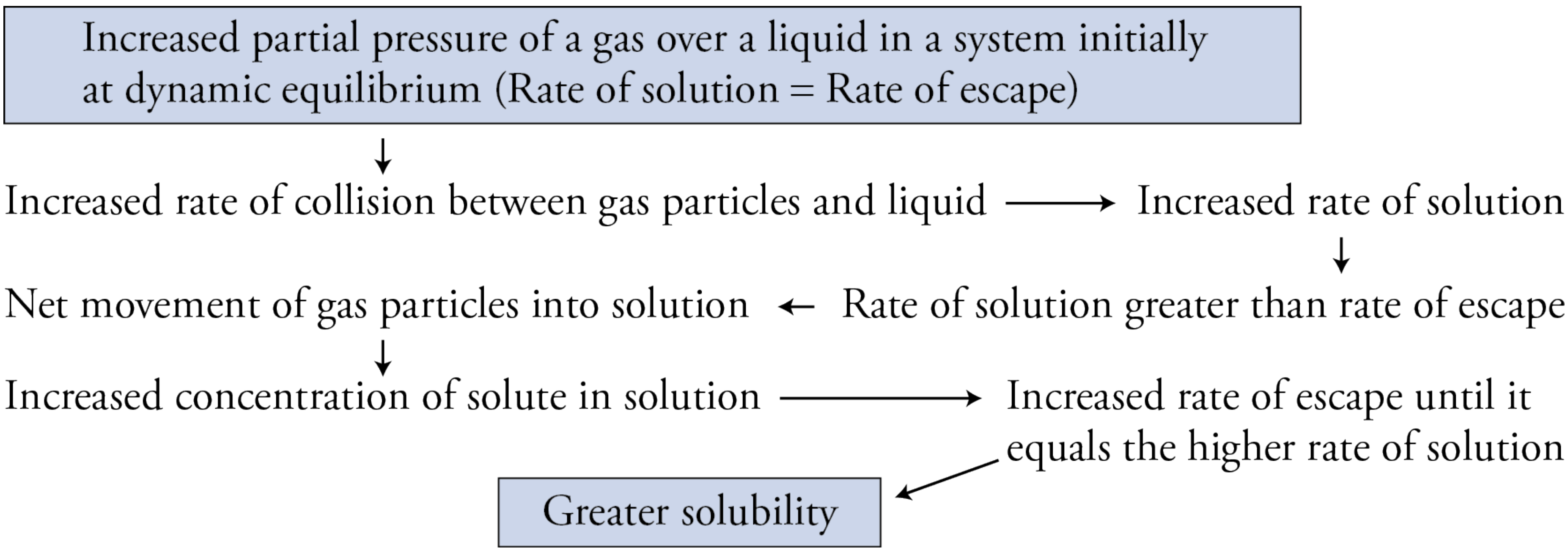
Dynamic Equilibrium for Gas Dissolved in Liquid

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



Oceanic Carbon

- One way that carbon enters the ocean is through solution of atmospheric CO_2.

  $$CO_2(g) \rightleftharpoons CO_2(aq)$$

- 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 $R_{soln} > R_{escape}$,
  - and leading to a net shift of CO_2 into the ocean.

CO_2 and Ocean Acidity

- CO_2 molecules react with water to form carbonic acid.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

CO_2 and Ocean Acidity

- 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.

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$

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

$$H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$

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.