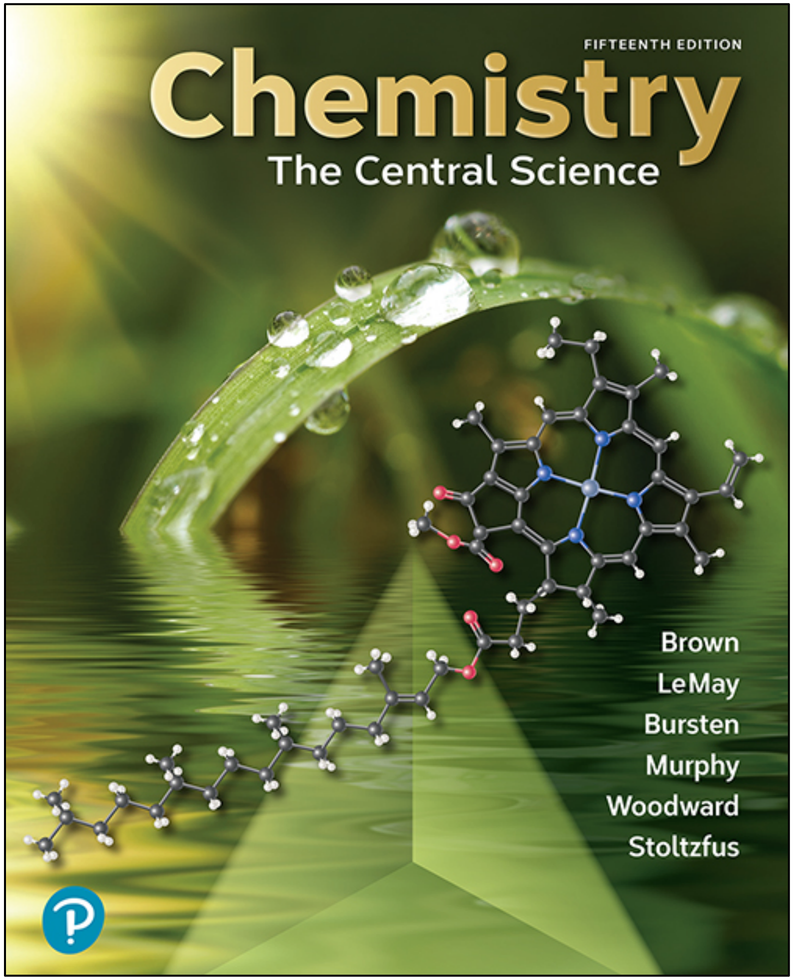
Chemistry: The Central Science

Fifteenth Edition



Chapter 13

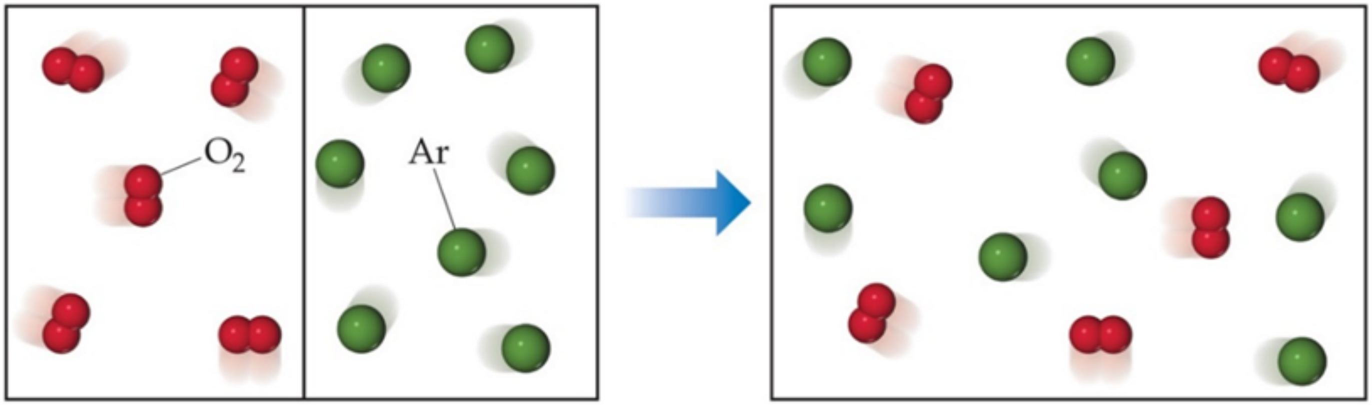
Properties of Solutions

13.1 The Solution Process

- **Solutions** are homogeneous mixtures of two or more substances.
- In a solution, the **solute** is dispersed uniformly throughout the **solvent**.
- The ability of substances to form solutions depends on
  - natural tendency toward mixing.
  - intermolecular forces.

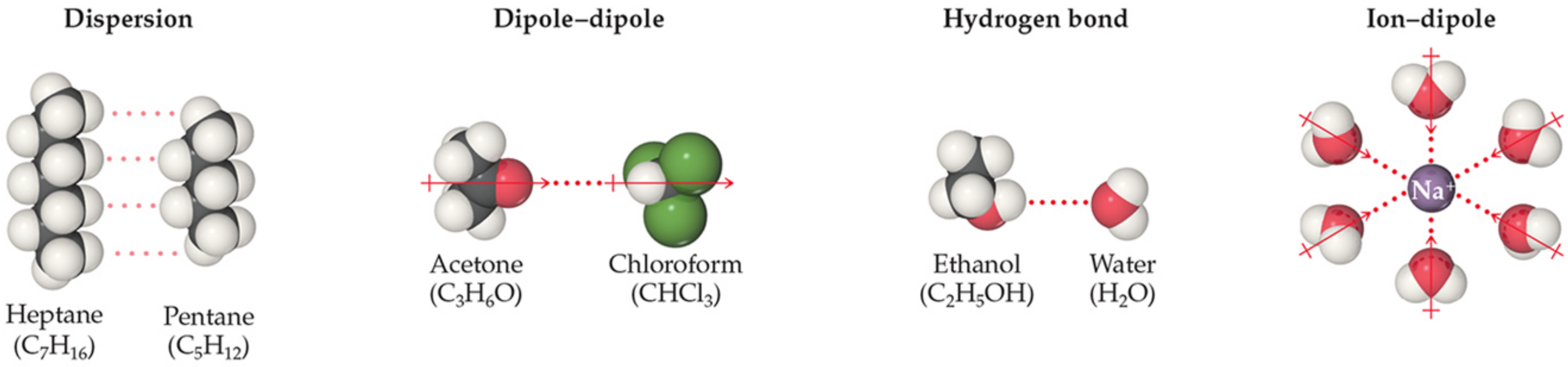
Why is there a Natural Tendency Toward Mixing

- Mixing of gases is a **spontaneous** process.
- Each gas acts alone to fill the container.
- Mixing causes **more randomness** in the position of the molecules,
- **Increasing entropy**.
- The formation of solutions is favored by the increase in **entropy** that accompanies mixing.



Intermolecular Forces and solutions

- intermolecular forces will operate between different molecules.
- solute and solvent molecules (Chapter 11).



Intermolecular Forces and solutions

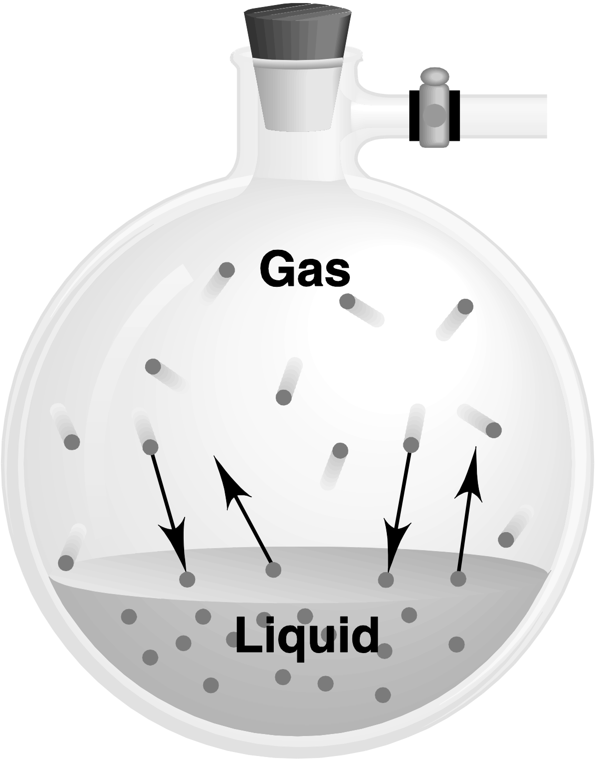
- Three possibilities:

1. **Solute–solute interactions** must be overcome to disperse the particles through the solvent.
2. **Solvent–solvent interactions** must be overcome to make room for the solute particles in the solvent.
3. **Solvent–solute interactions** between the solute and solvent particles occur as the particles mix.

Chapter 11, Vapor pressure

Imagine a liquid in a closed container with a perfect vacuum above the liquid.

Then, stop the vacuum pump.
The liquid will **evaporate** to a certain extent, then stop.
The resulting pressure is the VAPOR PRESSURE of the liquid.



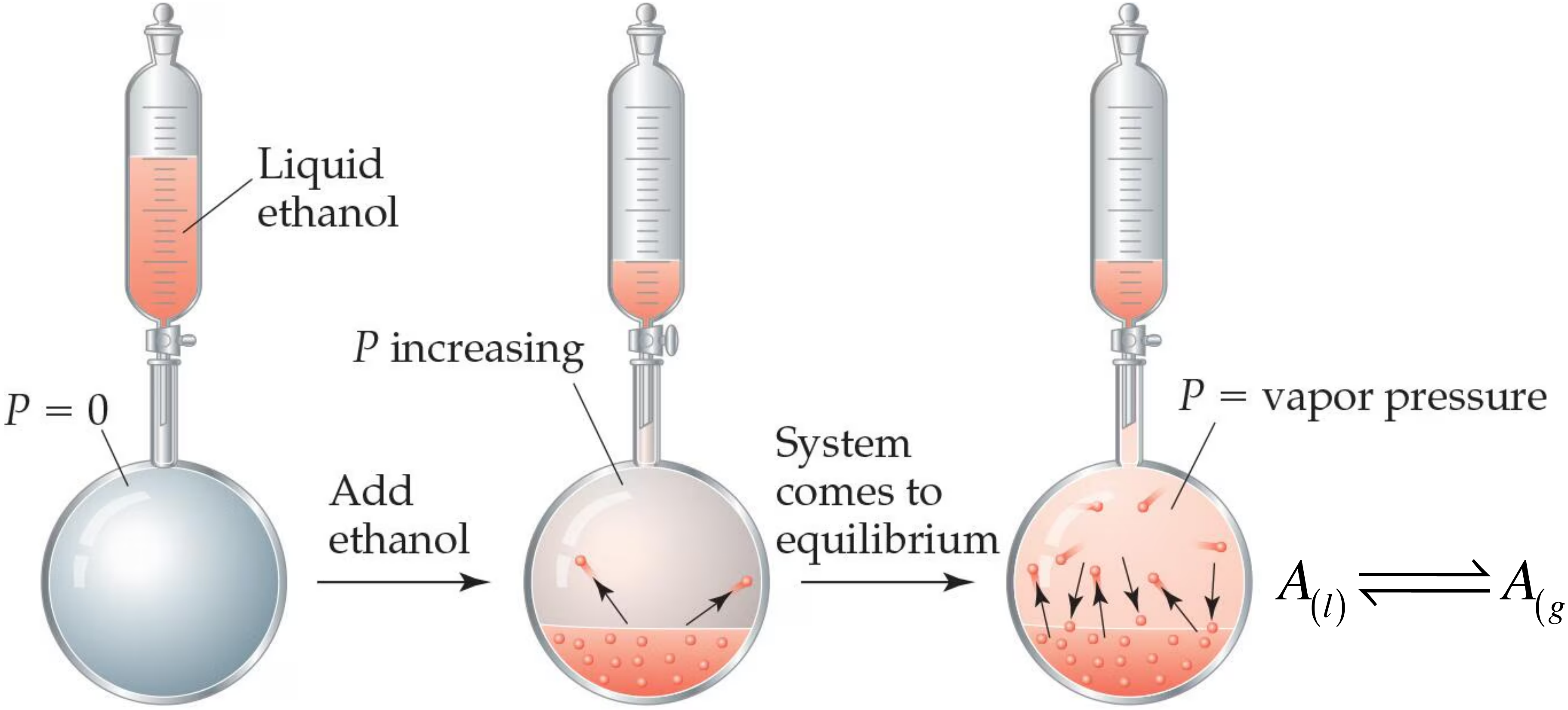
VAPOR PRESSURE:

The characteristic pressure in the gas phase when the liquid-gas phase equilibrium has been reached.

$$A_{(l)} \rightleftharpoons A_{(g)}$$

Different liquids have different vapor pressures at a given temperature, **depending on the strengths of the intermolecular forces** between liquid-phase molecules.

Chapter 11, Vapor pressure



$$A_{(l)} \rightleftharpoons A_{(g)}$$

Evacuated flask, pressure zero

Molecules begin to vaporize, pressure increases

Molecules leave and enter liquid at equal rates, pressure reaches steady-state value

Chapter 11, Boiling point

Vapor pressure always increases with temperature
More kinetic energy, more molecules escape from the liquid phase

What is boiling? ***vapor pressure = the atmospheric pressure,***
the liquid phase is no longer a stable phase and the liquid boils.

The **Normal Boiling Point:** temperature at which the vapor pressure of that liquid is precisely **1 atm.**

Weak intermolecular forces (dipole-dipole)

Strong intermolecular forces (H-bonding)

Very strong intermolecular forces (Dispersion)

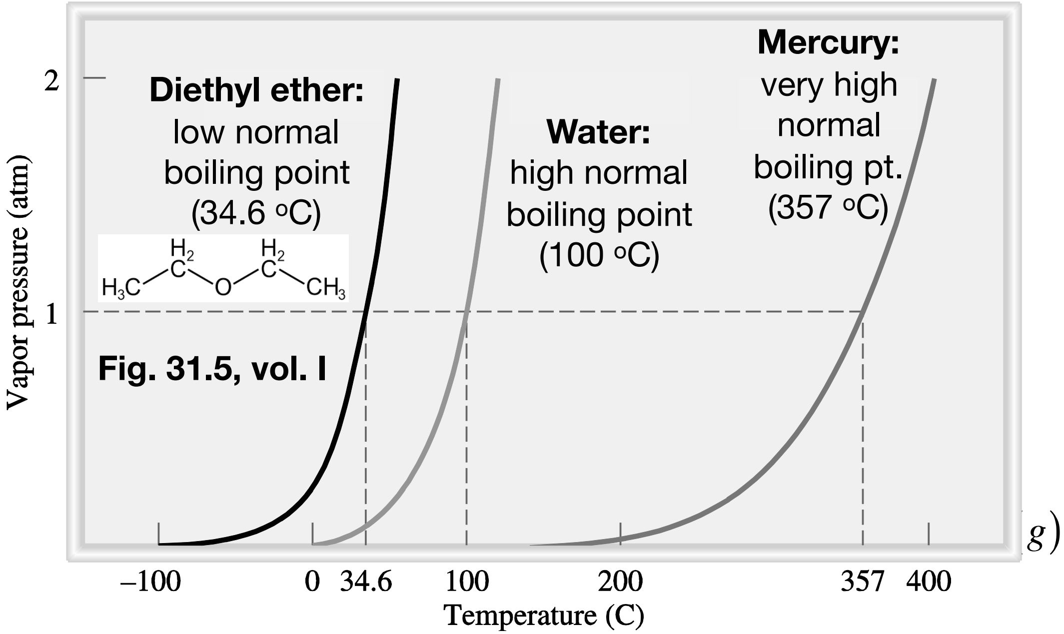
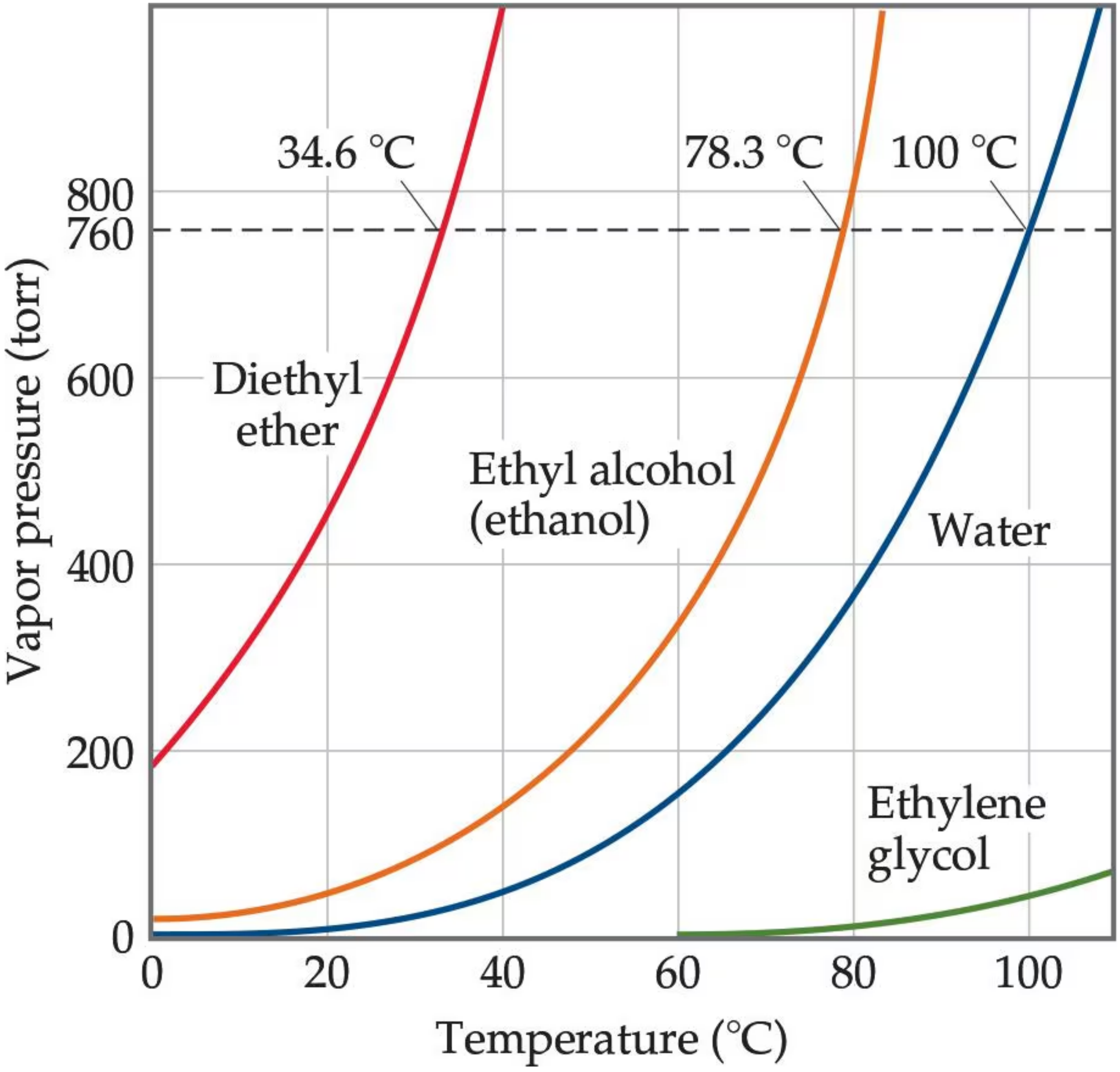


Fig. 31.5, vol. I

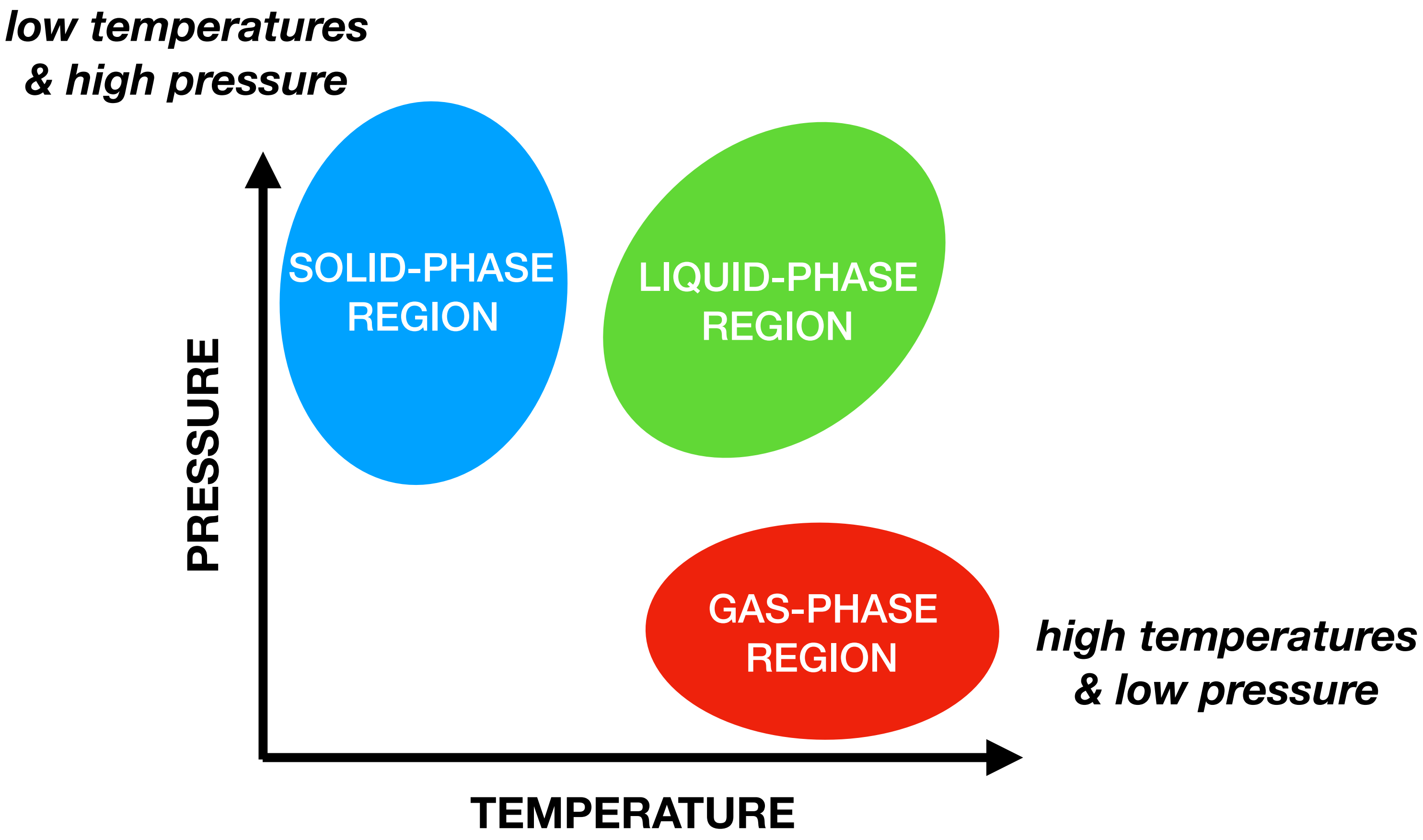
If atmospheric pressure is lower:
Boiling point is lower.
(for example, on top of a high mountain)

Chapter 11, Boiling point



Chapter 11, Phase diagram

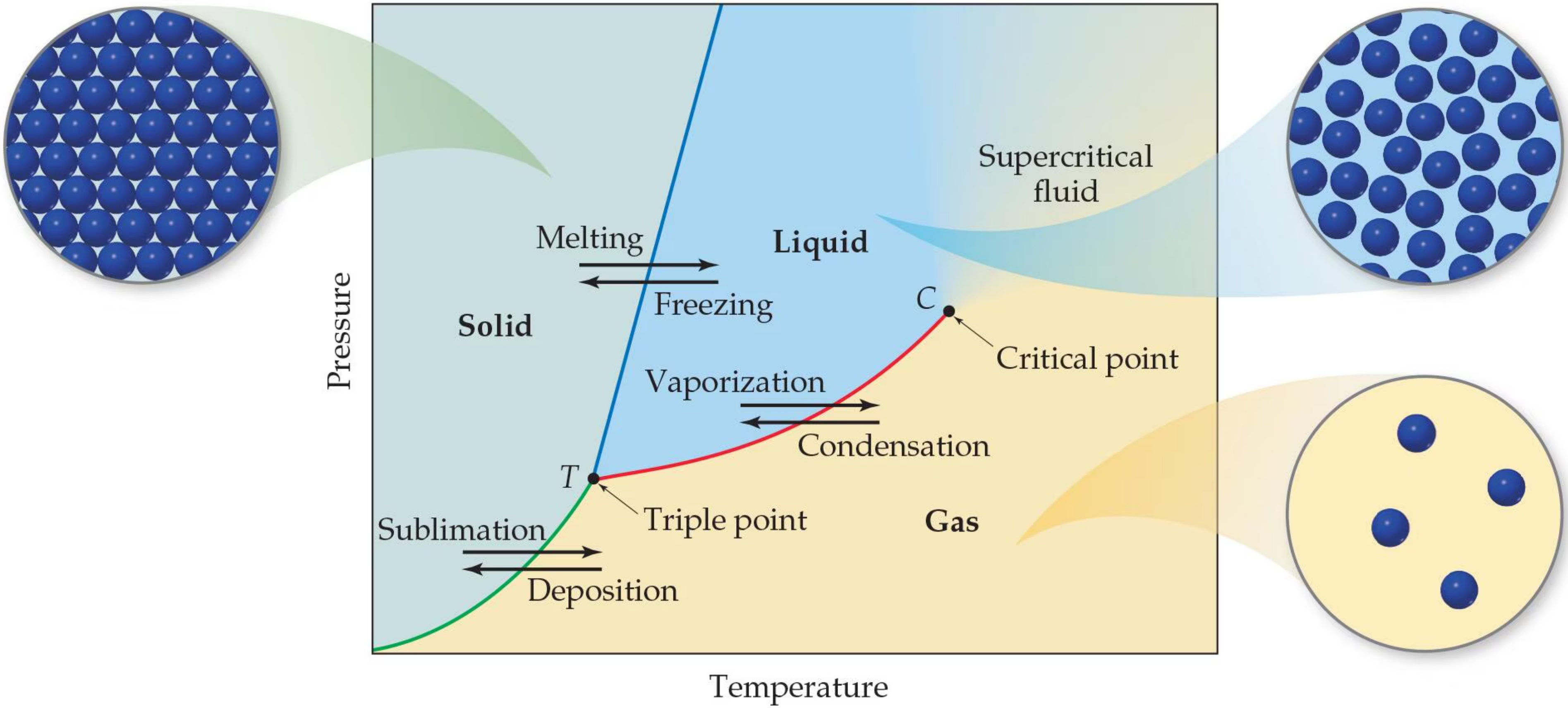
Phase Diagram: A “map” that shows the conditions under which the different phases of matter (solid, liquid, gas) are stable



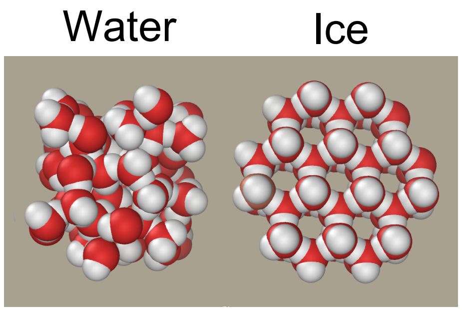
Chapter 11, Phase diagram

- ***At least three “lines” (straight or curved)*** to separate the three regions.
- One common point **(“TRIPLE-POINT”)** where all three lines meet.
- One additional point at the end of the line separating the liquid and gas phase **(“CRITICAL” POINT)**.

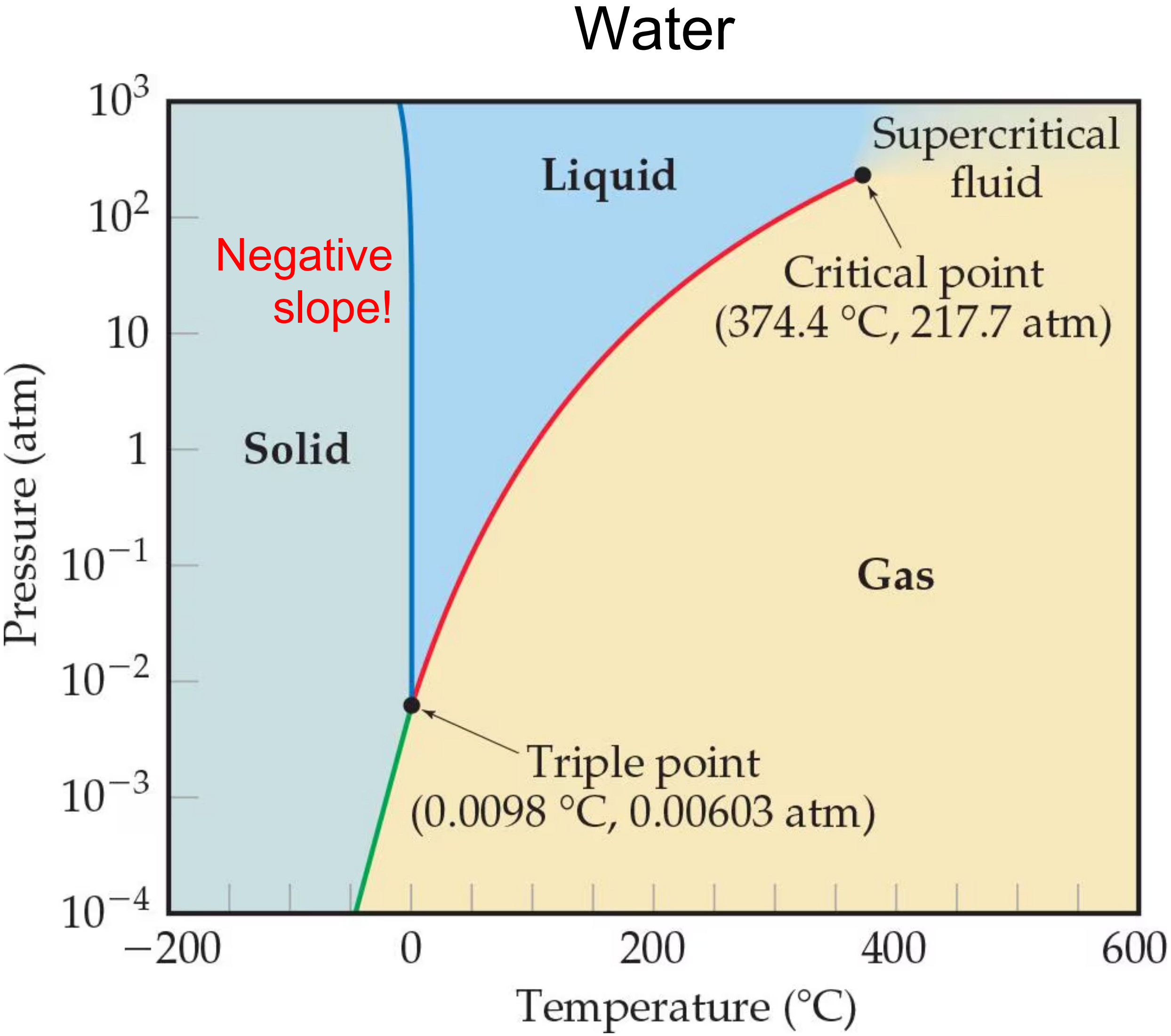
Phase diagram of ”typical” matter



Chapter 11, Phase diagram



The solid is LESS dense than the liquid phase.



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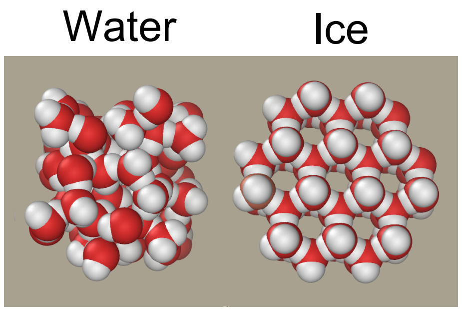

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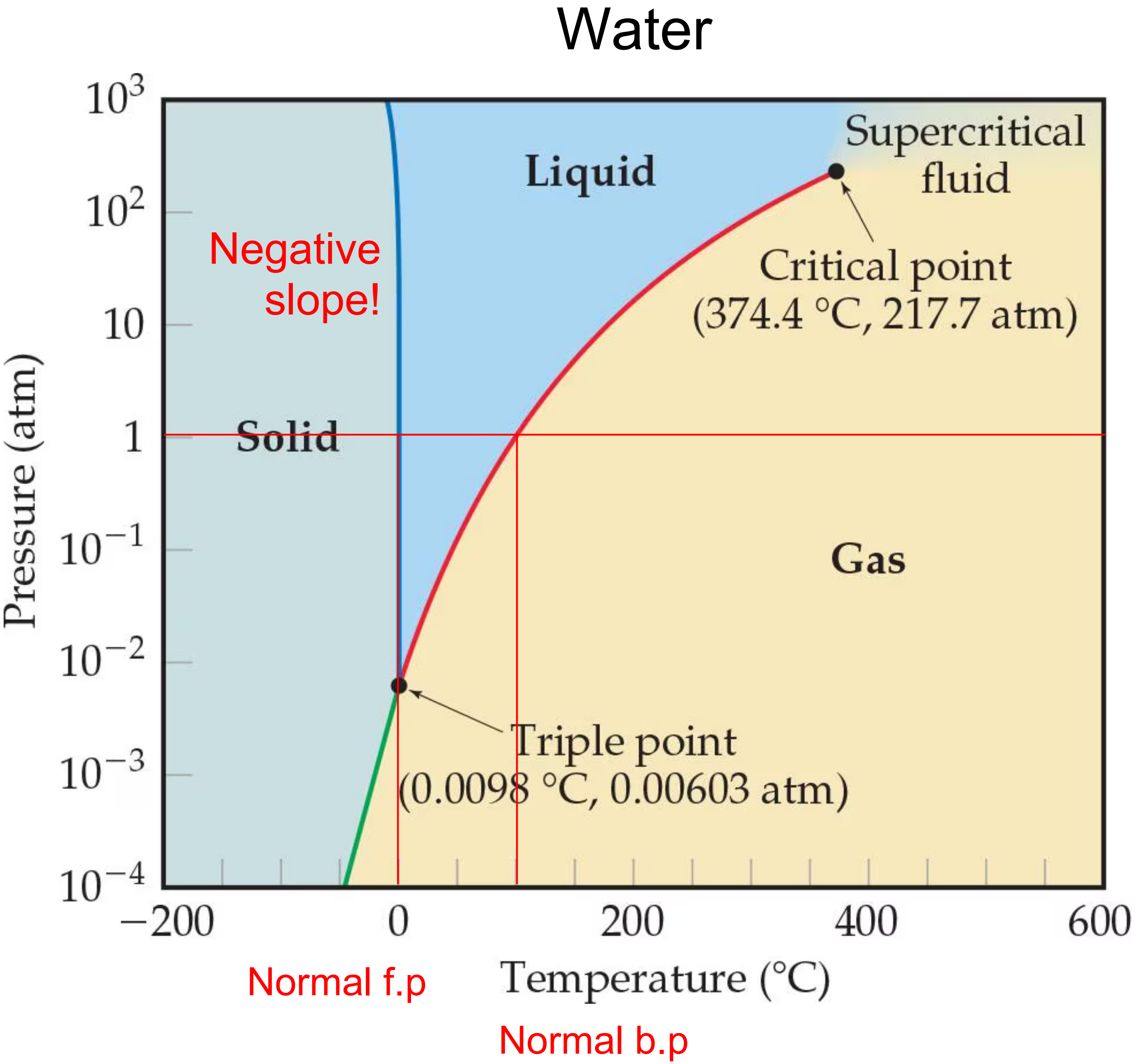
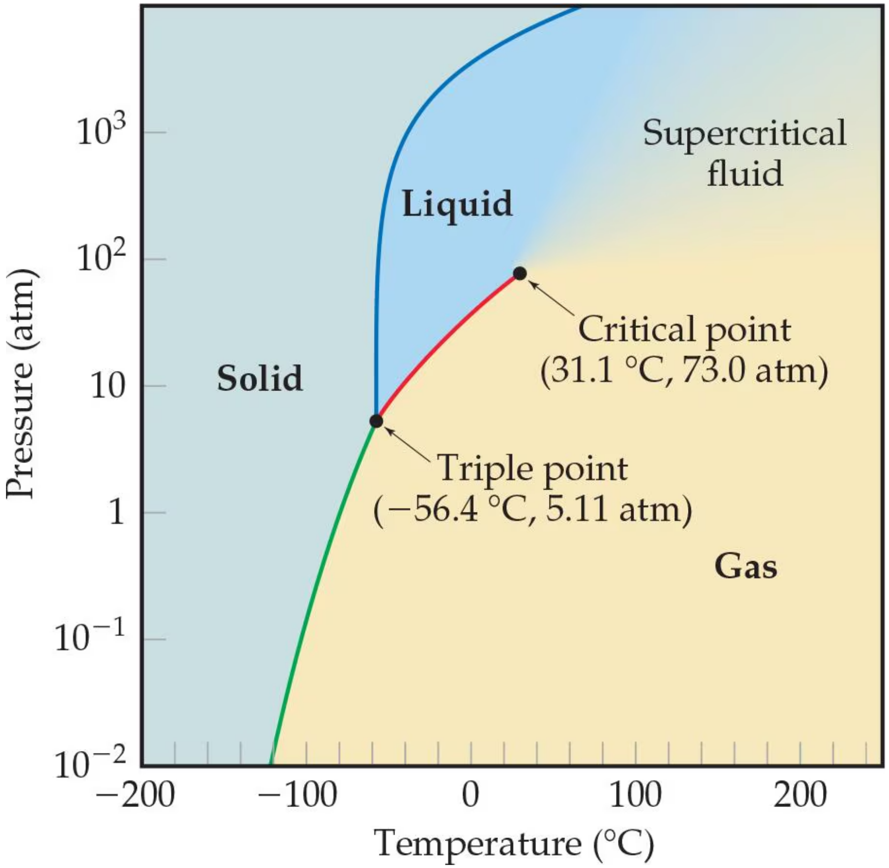


Chapter 11, Phase diagram

CO_2



Usually, solid has a LARGER density than liquid (this is the case for CO_2).

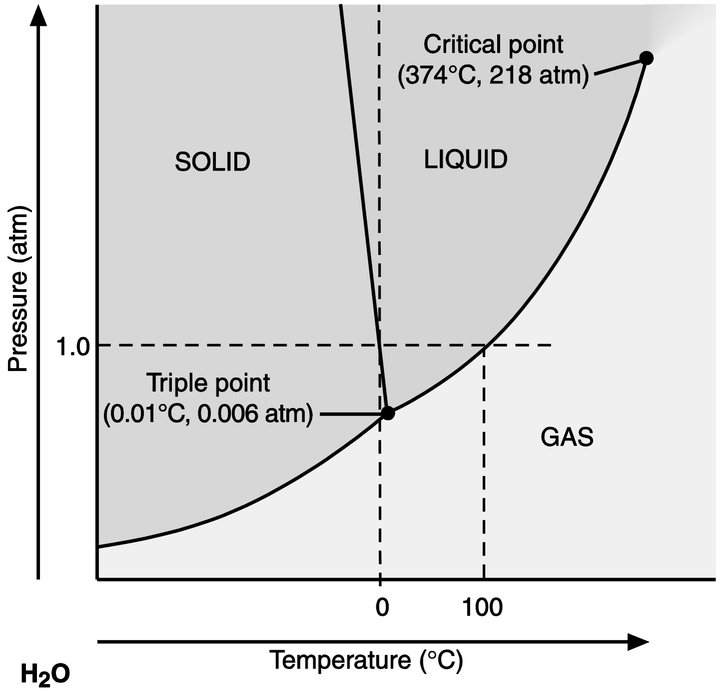
The triple point is HIGHER than 1 atm: we cannot form liquid CO_2 at normal pressures.

CO_2 goes from the solid directly to the gas phase (“sublimes”) above 195 K (-78 °C) at 1 atm.

Phase Diagrams

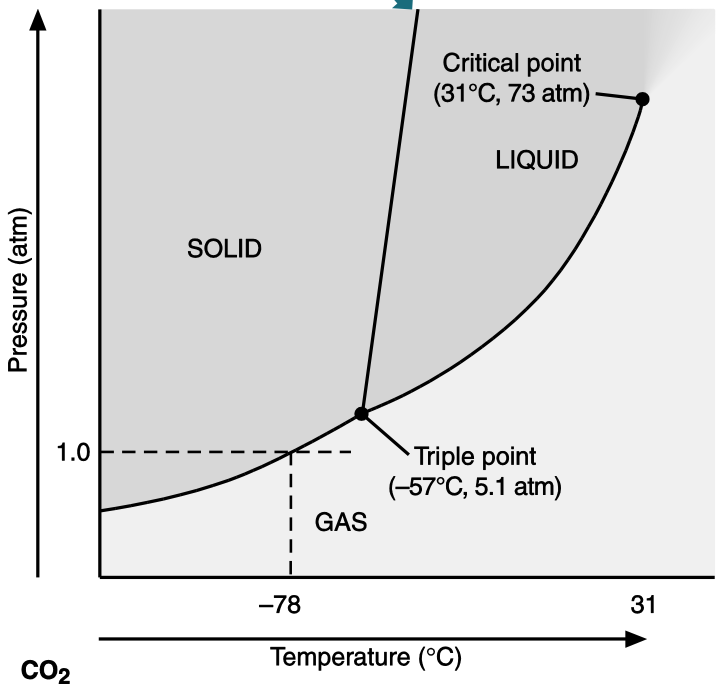
Water (H_2O)

The NEGATIVE slope
of the solid-liquid line.



Carbon dioxide (CO_2)

Positive slope



Back to Chapter 13

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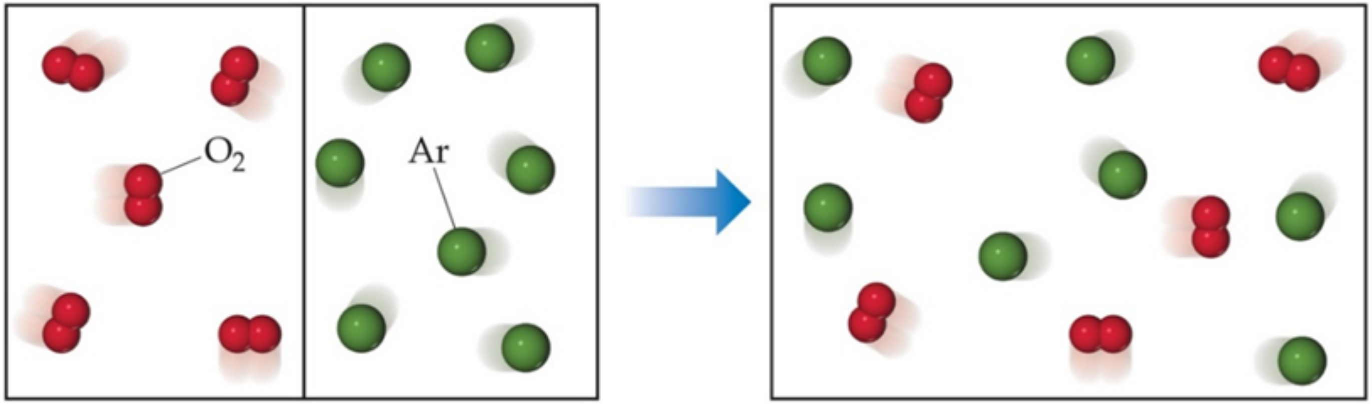

Intermolecular Forces and solutions

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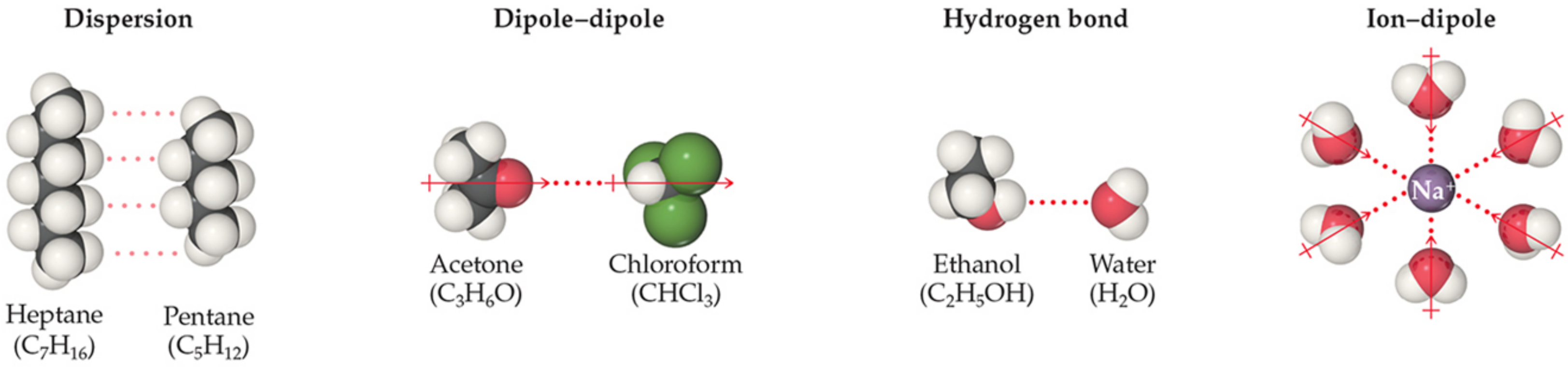
- solute and solvent molecules.



Intermolecular Forces and solutions

- Three possibilities:

1. **Solute–solute interactions** must be overcome to disperse the particles through the solvent.
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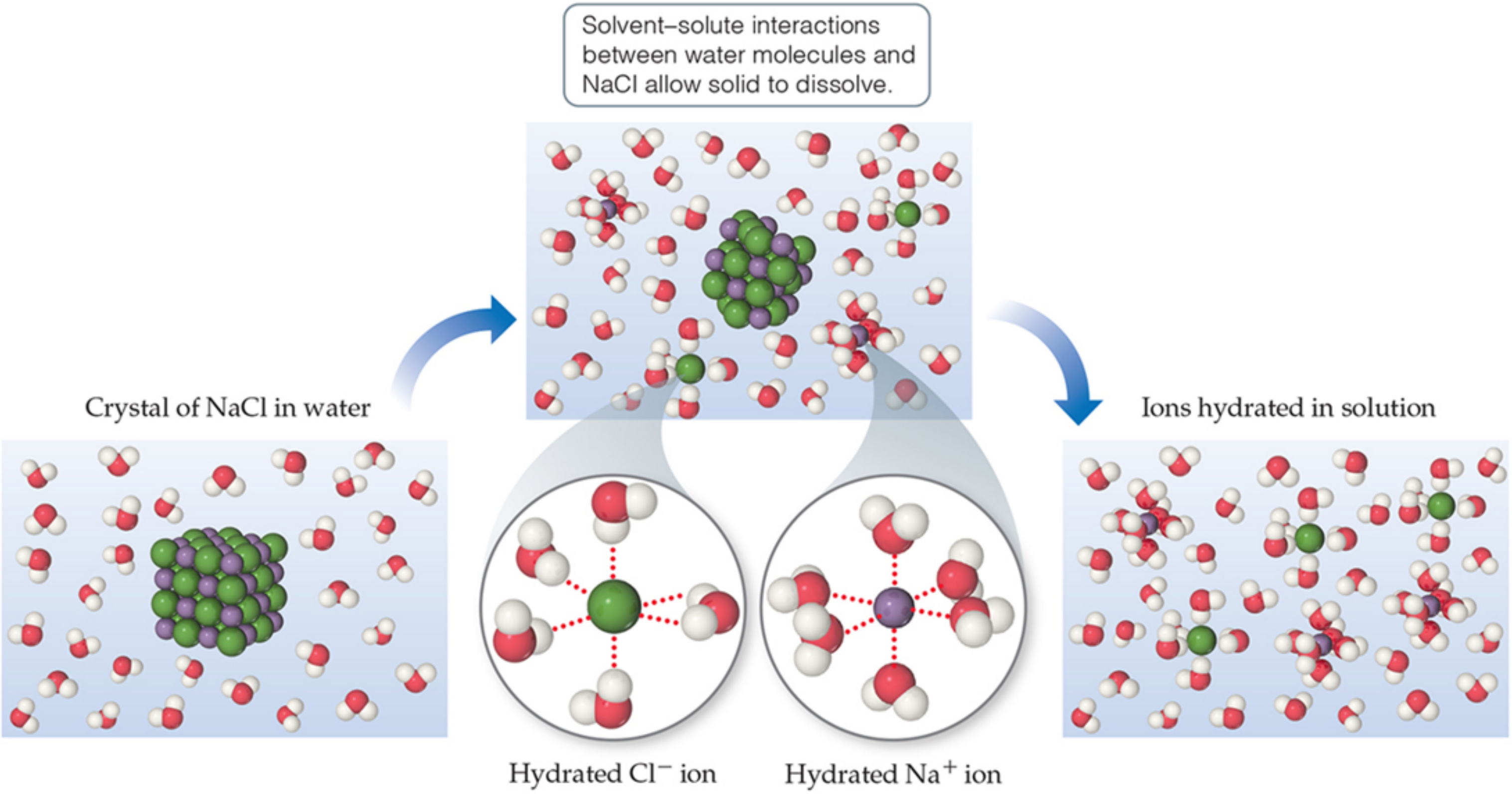
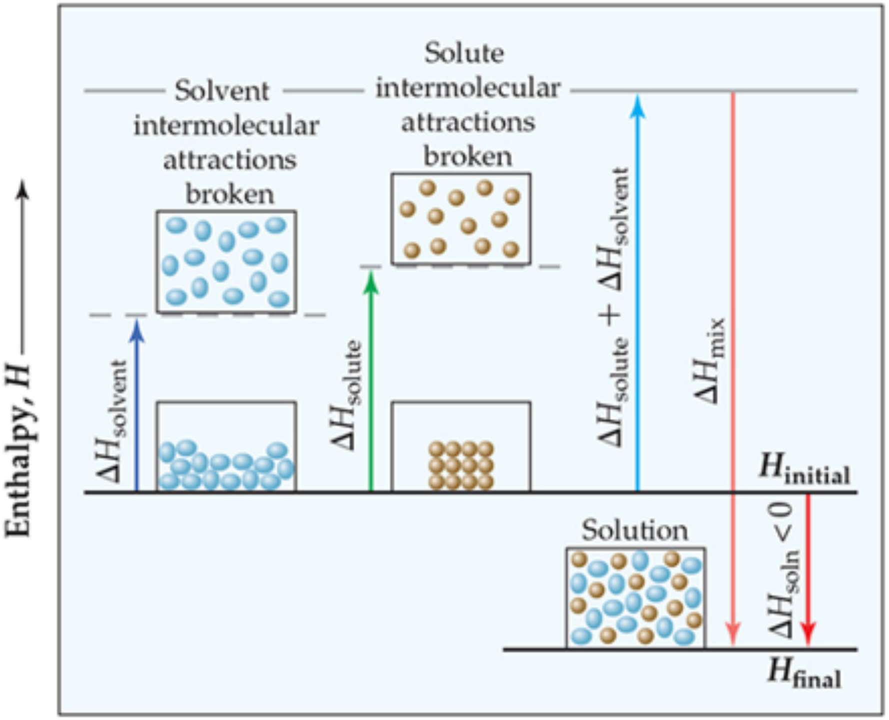
Dispersion of an Ionic Solid in Water

- When the solvent is water, the interactions are referred to as hydration.
- The phase designation is (aq) for the ions.

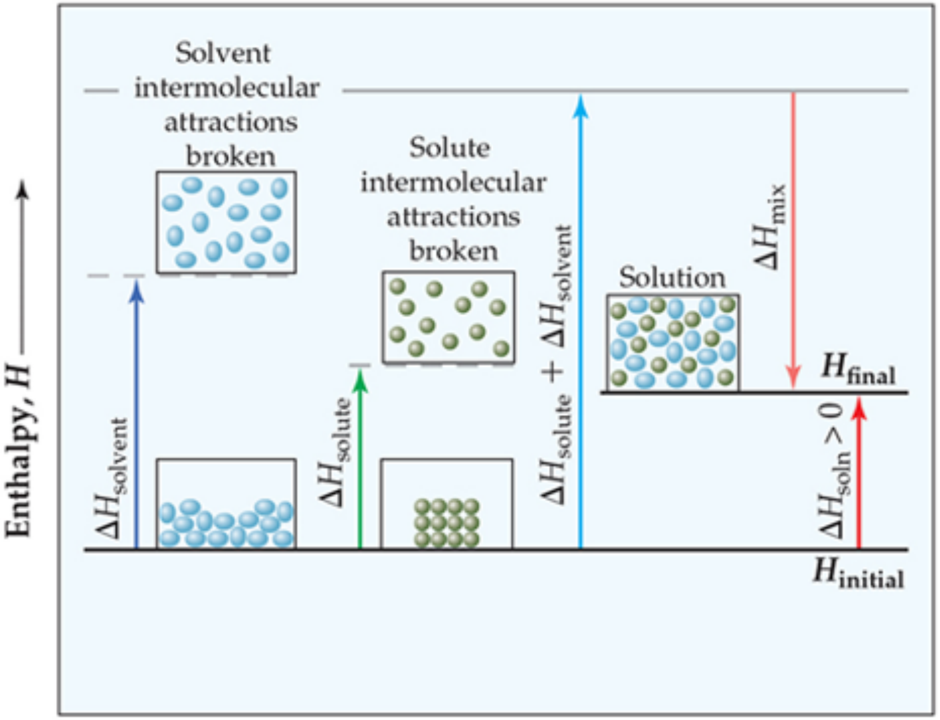


Energetics of Solution Formation

- **Exothermic** solution formation is ***always*** spontaneous.
- For endothermic solution:
  - ΔH_{mix} must be close to $\Delta H_{solute} + \Delta H_{solvent}$



Exothermic solution process



Endothermic solution process

Caution! Dissolution vs Chemical Reactions

- Chemical reaction: If a substance disappears when it comes in contact with a solvent, it does not mean the substance dissolved. It may have reacted, like nickel(s) with hydrochloric acid to produce Ni^{2+} (aq) and $H_2(g)$.

Nickel metal and hydrochloric acid

Nickel reacts with hydrochloric acid, forming $NiCl_2(aq)$ and $H_2(g)$. The solution is of $NiCl_2$, not Ni metal

$NiCl_2 \cdot 6\,H_2O(s)$ remains when solvent evaporated

13.2 Saturated Solutions and Solubility

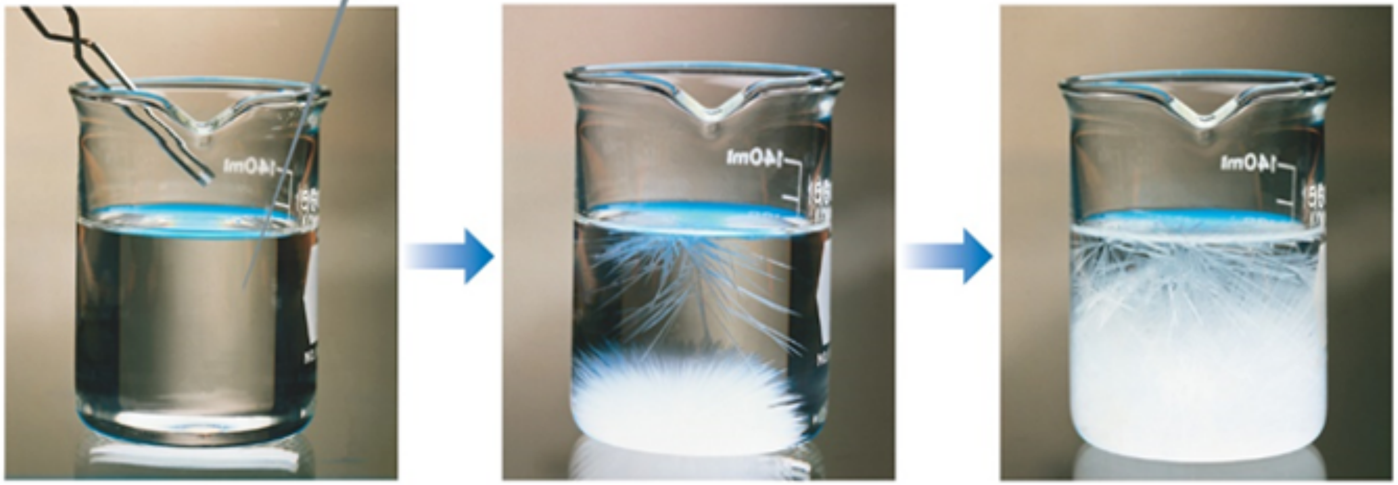
- The solution-making process and crystallization are opposing processes. They are temperature dependent.

$$\text{solute} + \text{solvent} \underset{\text{crystallize}}{\overset{\text{dissolve}}{\rightleftarrows}} \text{solution}$$

- When the rate of precipitation = rate of dissolving
  - **equilibrium** is established. Additional solute will not dissolve. This is a **saturated** solution.
- **The maximum amount that will dissolve is the solubility** of the solute.
- If less solute is dissolved than needed to form a saturated solution, the solution is **unsaturated**.

Supersaturated Solutions

Amount of sodium acetate dissolved is greater than its solubility at this temperature.



1 Seed crystal of sodium acetate is added to supersaturated solution.

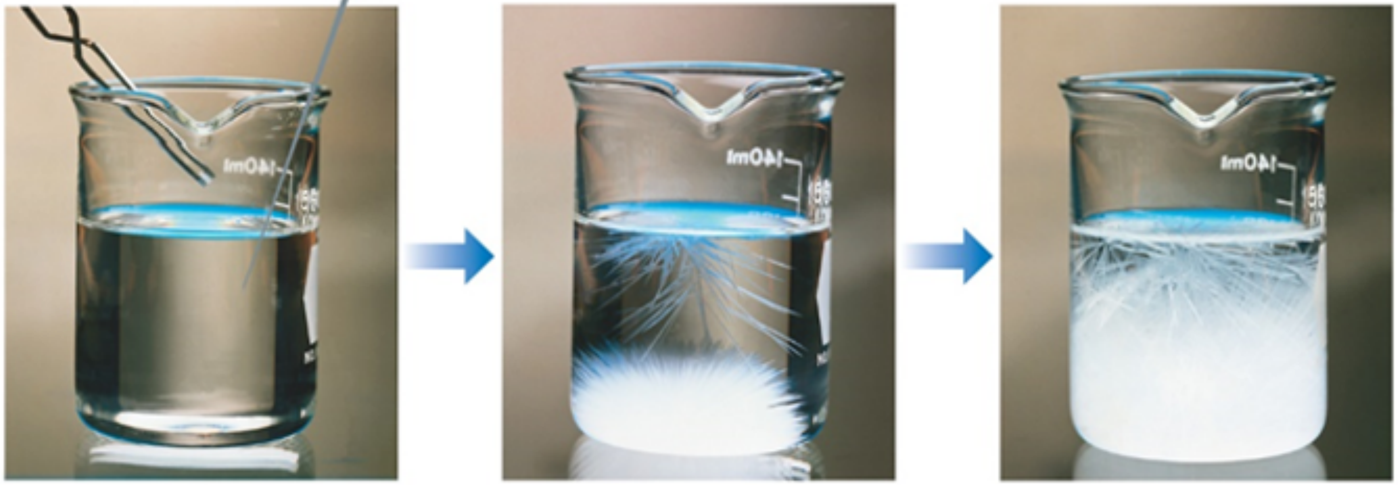
2 Excess sodium acetate starts to crystallize from solution.

3 Solution is saturated and excess solute has crystallized.

- These are uncommon solutions.
- In **supersaturated** solutions, the solute concentration is higher than saturated.
- ΔG of precipitation is *negative*
- ***Why??***

Supersaturated Solutions

Amount of sodium acetate dissolved is greater than its solubility at this temperature.



① Seed crystal of sodium acetate is added to supersaturated solution.

② Excess sodium acetate starts to crystallize from solution.

③ Solution is saturated and excess solute has crystallized.

- In **supersaturated** solutions, the solute concentration is higher than saturated.
- ΔG of precipitation is *negative*
- ***Why??***
- ***Kinetics. Crystallization rate is slow, there is a barrier.***
- ***Adding a seed crystal is like a catalyst. Increases rate of crystallization.***

13.3 Factors That Affect Solubility

- The extent to which one substance dissolves in another depends on the nature of both substances.
- "**Like dissolves like**" refers to intermolecular forces.
- Polar liquids tend to dissolve readily in polar solvents. Polar solvents have D (dipole) and/or HB (hydrogen bonding) intermolecular forces.

  Water (HB, D) and acetone (D) mix.
- Nonpolar liquids tend to dissolve readily in nonpolar solvents.

  Hexane (London) and heptane (London) mix.
- Water (HB, D) and hexane (L) do not mix.

Solute–Solvent Interactions

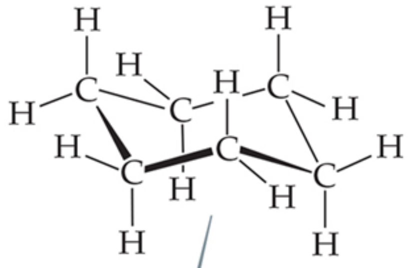
- The **stronger** the solute–solvent interaction, the **greater** the solubility of a solute in that solvent.
- There are exceptions, but a rule of thumb: Molecules containing only C and H tend to be nonpolar. Molecules containing N, O, S, and P tend to be polar.
- As for gases in water, the larger the gas, the more soluble it will be in water.

Table 13.1 Solubilities of Gases in Water at 20°C, at 1 atm Gas Pressure

Gas	**Molar Mass** $(\mathbf{g/mol})$	**Solubility (*M*)**
N_2	28.0	0.69×10^{-3}
O_2	32.0	1.38×10^{-3}
Ar	39.9	1.50×10^{-3}
Kr	83.8	2.79×10^{-3}

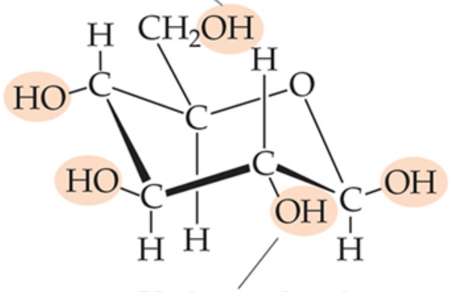
Organic Molecules in Water

- Polar organic molecules dissolve in water better than nonpolar organic molecules.
- As the number of –OH along the carbon chain increases, HB increases, the solubility in water will increase.

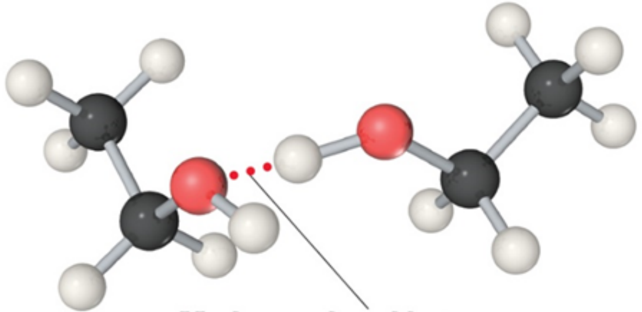


Cyclohexane, C_6H_{12}, which has no polar OH groups, is essentially insoluble in water.

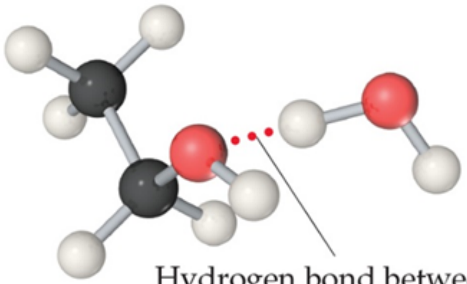
In glucose, the OH groups enhance the aqueous solubility because of their ability to hydrogen-bond with H_2O.



Hydrogen-bonding sites



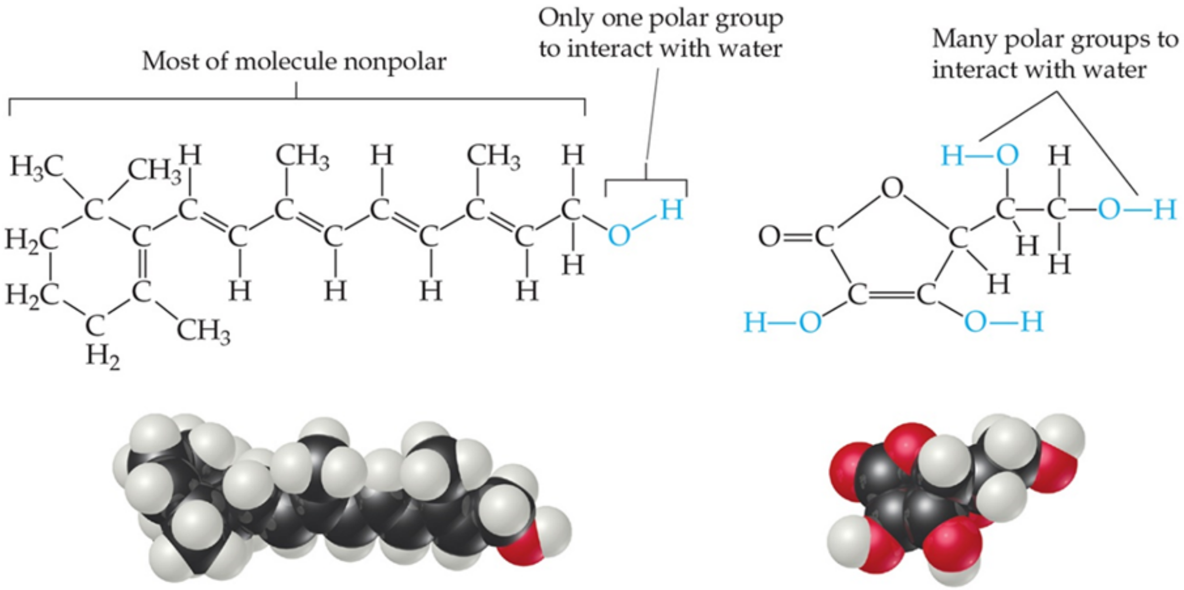
Hydrogen bond between two ethanol molecules



Hydrogen bond between ethanol molecule and water molecule

Solubility and Biological Importance

- Fat-soluble vitamins (like vitamin A) are nonpolar; they are readily stored in fatty tissue in the body.
- Water-soluble vitamins (like vitamin C) need to be included in the daily diet.

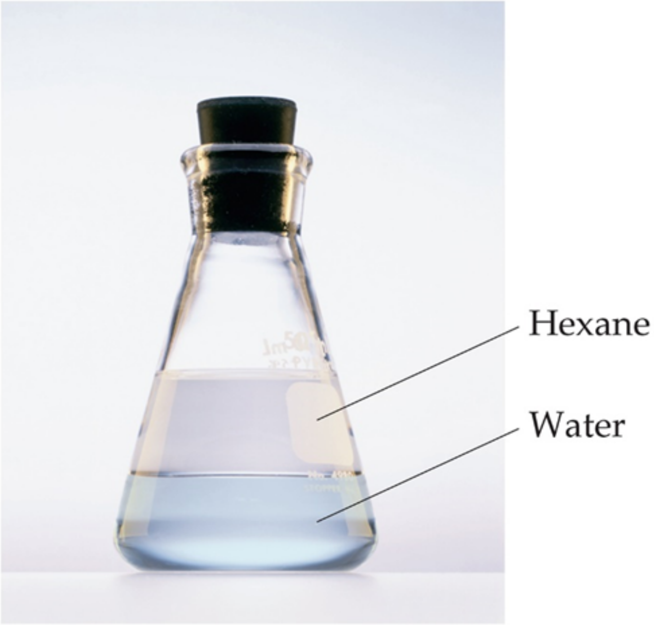


Vitamin A

Vitamin C

Liquid/Liquid Solubility

- Liquids that mix in all proportions are **miscible**.
- Liquids that do **not** mix in one another are **immiscible**.
- Because hexane is nonpolar and water is polar, they are immiscible.

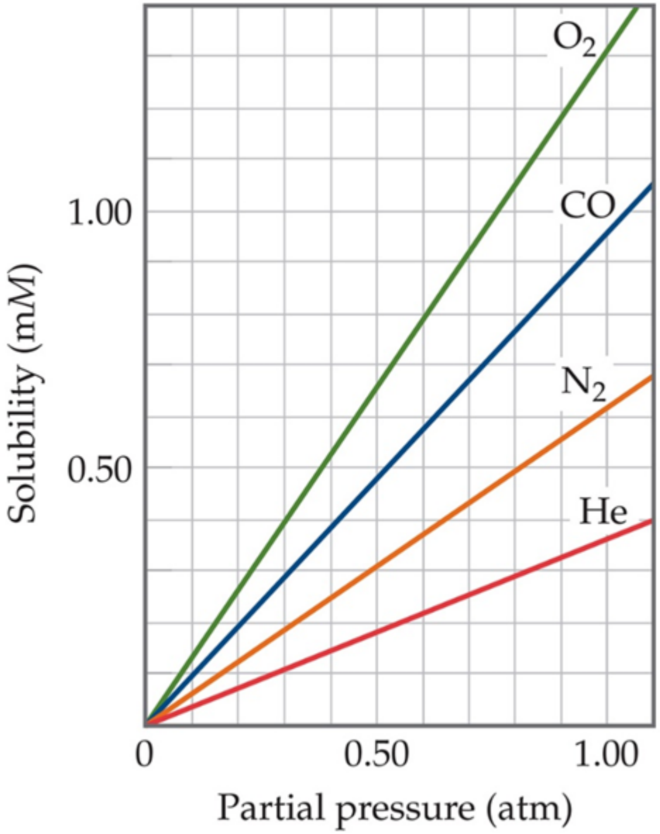


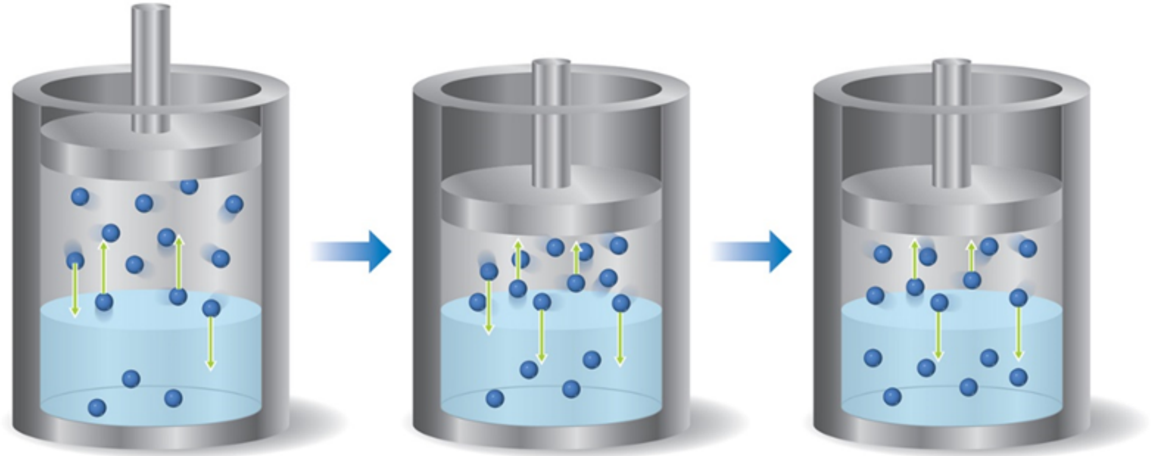
Pressure Effects

- The solubility of solids and liquids are **not** appreciably affected by pressure.
- Gas solubility is affected by pressure.

Henry’s Law

- The solubility of a gas (M) is proportional to the partial pressure of the gas above the solution.
- $S_g = kP_g$, k: Henry’s law constant





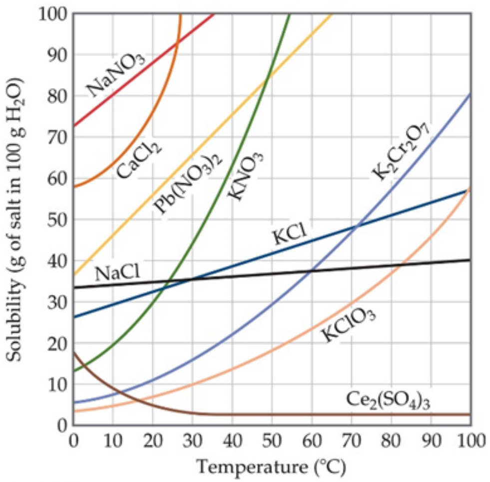
Equilibrium

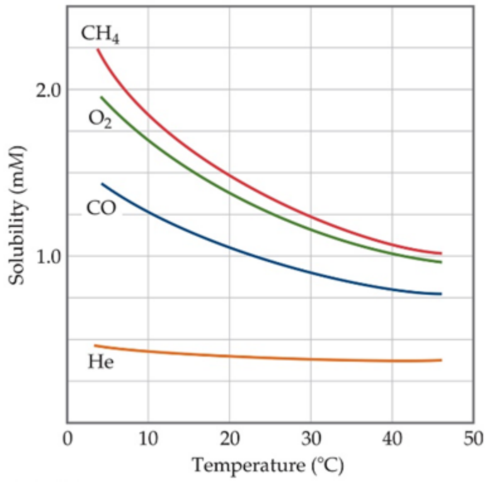
Pressure is increased. More CO_2 dissolves

Equilibrium restored

Temperature Effects

- For most solids, as temperature increases, solubility increases. However, clearly this is not always true—some increase greatly, some remain relatively constant, and others decrease.
- For **all** gases, as temperature increases, solubility decreases. Cold rivers have higher oxygen content than warm rivers.





13.4 Expressing Solution Concentration

- Solutions may be considered as dilute or concentrated (low or high concentration).
- Quantitative measurements are also needed.
- Mass and volume are used to calculate:
  - mass percent
  - ppm, ppb
  - mole fraction
  - Molarity
  - molality

Mass Percentage

- Percent means “out of 100.”
- Take the ratio of the mass of the each component to the total solution mass.
- Multiply by 100 to make it a percent.

$$\text{Mass \% of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$$

Parts per Million (ppm) and Parts per Billion (ppb)

- Relates mass of a solute to the total mass of the solution.
- If percent is out of 100, multiply by 100.
- ppm is per million, so multiply by 10^6.

$$\text{ppm of component} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$$

- ppb is parts per billion so instead multiply by 10^9

Mole Fraction (χ)

- Mole fraction is the ratio of moles of the component to the total number of moles in a solution.
- Moles of both solute and solvent are used.

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}}$$

Molarity (M) and Molality (m)

- Molarity was discussed in Chapter 4 as moles of solute per liter of solution.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of soln}}$$

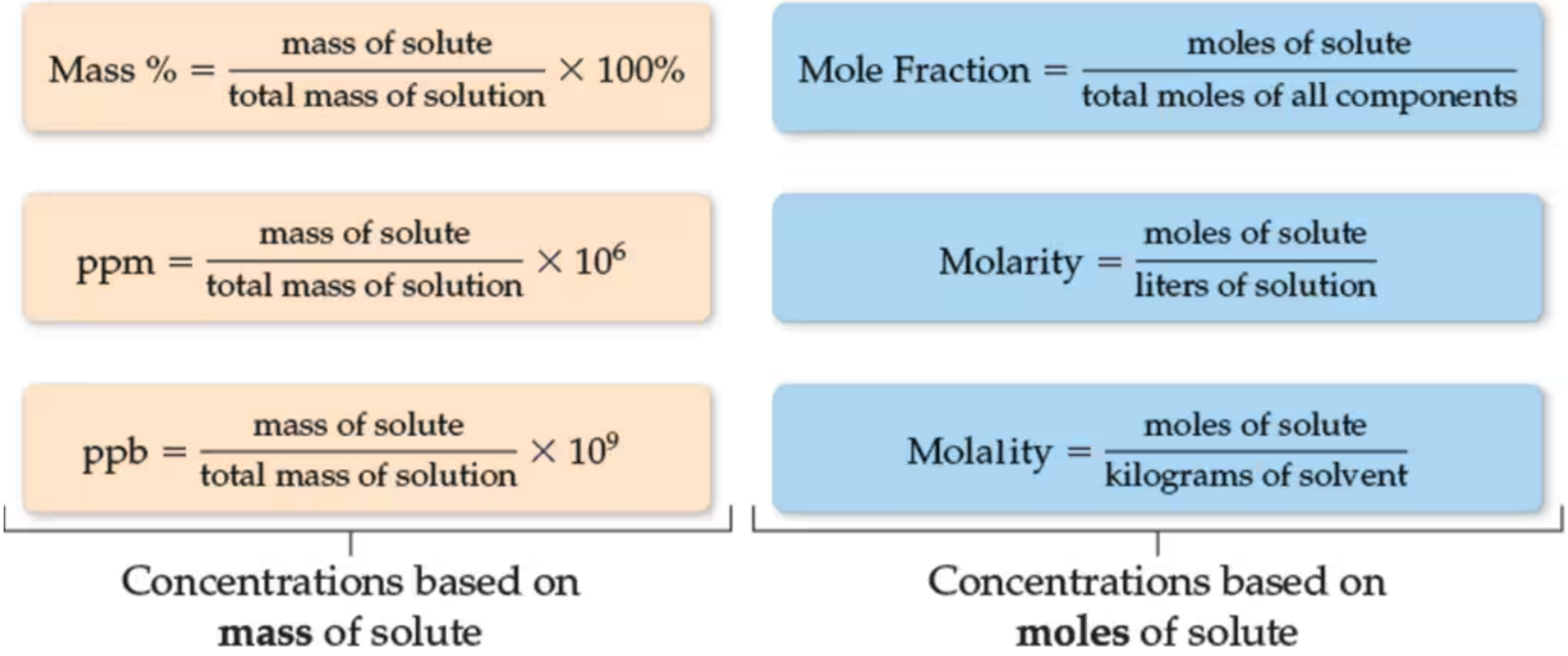
- Molality is moles of solute per kilogram of solvent.

$$\text{Molality} = \frac{\text{moles of solute}}{\text{Kilograms of solvent}}$$

Molarity(M) versus Molality(m)

- When water is the solvent, dilute solutions have similar Molarity (M) and molality (m).
- If solutions are more concentrated, there will be a notable difference.
- With Molarity (M), volume may change with temperature. Mass does not change. So Molarity will change with temperature.
- molality (m) is mass based. It does not vary with temperature. Will be used with colligative properties. It is also more convenient when large quantities are used.

Concentrations summary



$$\text{Mass \%} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 100\%$$

$$\text{ppm} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 10^9$$

Concentrations based on **mass** of solute

$$\text{Mole Fraction} = \frac{\text{moles of solute}}{\text{total moles of all components}}$$

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Concentrations based on **moles** of solute

Converting Units

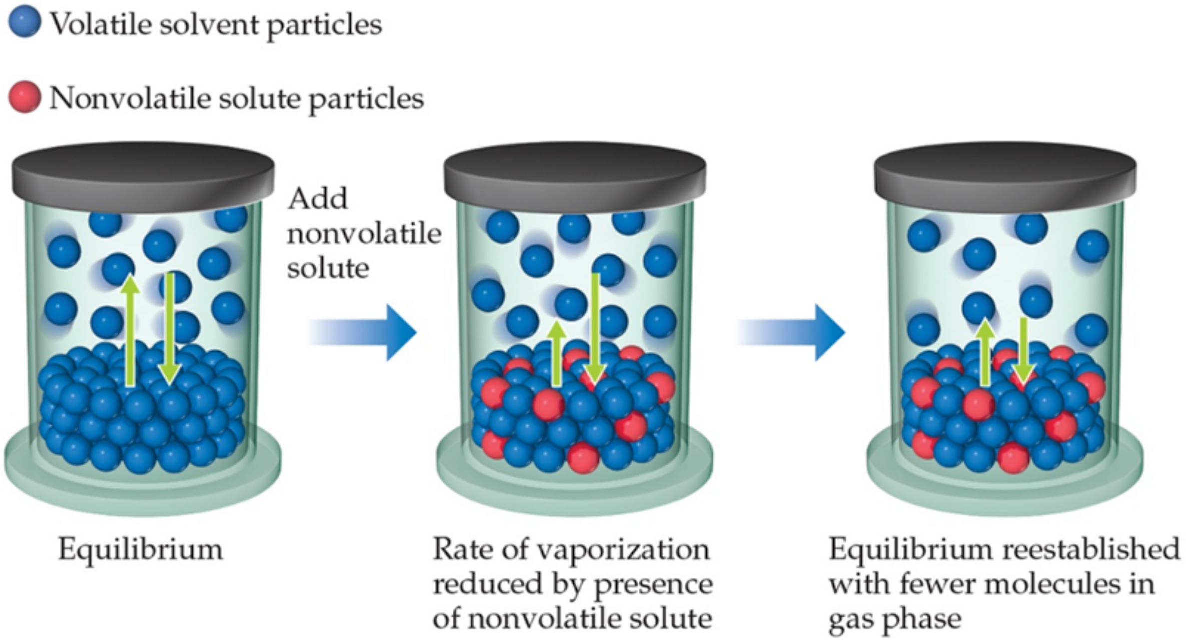
- Solution concentration calculations often require unit conversion.
- Follow dimensional analysis techniques from Chapter 1.
- To convert between molality and molarity, the density of the solution must be used.

13.5 Colligative Properties

- **Colligative properties** depend only on the **quantity**, not on the **identity** of the solute particles.
- Among colligative properties are
  - Vapor-pressure lowering
  - Boiling-point elevation
  - Freezing-point depression
  - Osmotic pressure

Vapor Pressure

- Pressure exerted by the vapor when it is in equilibrium with the liquid.
- Due to solute–solvent intermolecular attraction, solvent has a lower tendency to escape to the vapor phase.



Raoult’s Law

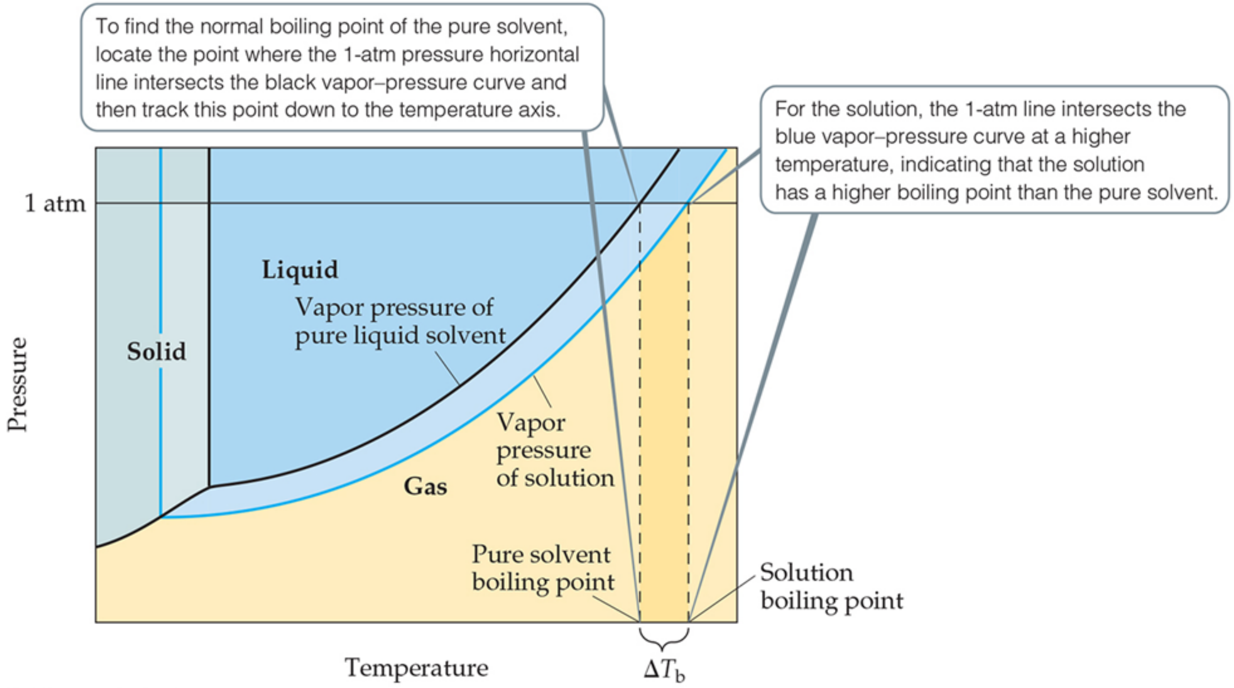
- The vapor pressure of a volatile solvent over the solution containing a nonvolatile solute is proportional to the solvent concentration in solution.
- Raoult’s Law describes this behavior. It is product of the mole fraction of the solvent times the vapor pressure of the pure solvent.

$$P_{\text{solution}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

- In ideal solutions, it is assumed that each substance will follow Raoult’s law while in the mixture.

Boiling-Point Elevation

- Vapor pressures are lower for solutions.
- A higher temperature is required to reach atmospheric pressure.
- Boiling point increases.

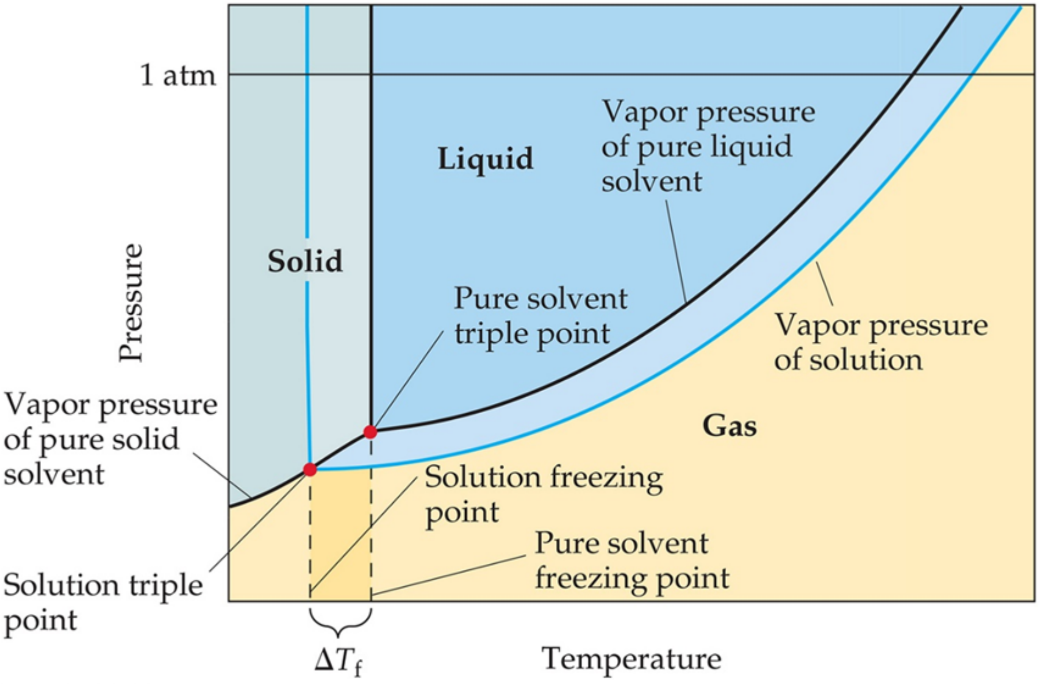


To find the normal boiling point of the pure solvent, locate the point where the 1-atm pressure horizontal line intersects the black vapor–pressure curve and then track this point down to the temperature axis.

For the solution, the 1-atm line intersects the blue vapor–pressure curve at a higher temperature, indicating that the solution has a higher boiling point than the pure solvent.

Freezing-Point Depression

- Freezing points are lower for solutions.
- A phase diagram for a solution confirms the freezing point is lowered while the boiling point is raised.



Calculating Boiling-Point Elevation and Freezing-Point Depression

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m$$

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m$$

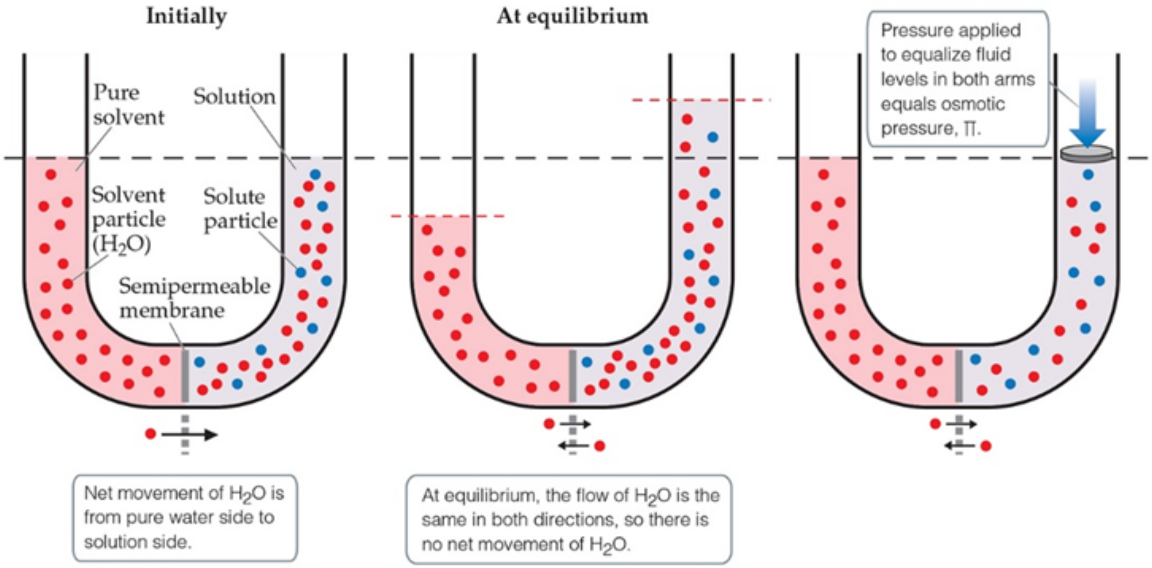
- The change in temperature $(^\circ\text{C})$ is directly proportional to molality.
- The van’t Hoff factor, *i*, is the number of particles present on dissolution.
- K_b and K_f are the solvent dependent molal boiling point and freezing point constants.

Table 13.3 Molal Boiling-Point-Elevation and Freezing-Point Depression Constants

Solvent	**Normal Boiling Point (°C)**	**K_b (°C / m)**	**Normal Freezing Point (°C)**	**K_f (°C / m)**
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	78.4	1.22	−114.6	1.99
Carbon tetrachloride, CCl_4	76.8	5.02	−22.3	29.8
Chloroform, $CHCl_3$	61.2	3.63	−63.5	4.68

Osmosis

- A **semipermeable membrane** allows selective passage of particles. Smaller particles pass through. Larger particles do not pass through.
- The net movement of solvent molecules from solution of low to high concentration of solute across a semipermeable membrane is **osmosis**. The applied pressure to stop it is **osmotic pressure**.



Pressure applied to equalize fluid levels in both arms equals osmotic pressure, Π.

Net movement of H_2O is from pure water side to solution side.

At equilibrium, the flow of H_2O is the same in both directions, so there is no net movement of H_2O.

Osmotic Pressure

- Osmotic pressure (symbol pi, atm) is a colligative property.

$$\prod = i\left(\frac{n}{V}\right)RT = iMRT$$

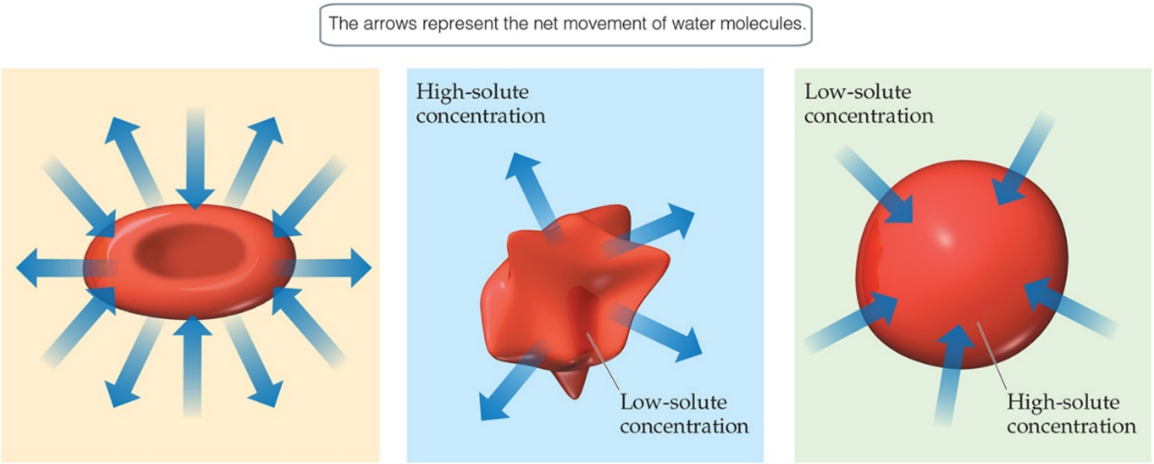
- Note calculation requires *i* (van Hof't factor), M (molarity), R (L atm/mol K), T (Kelvin).
- Once two solutions separated by a semipermeable membrane have the **same** osmotic pressure, no osmosis will occur.

Types of Solutions and Osmosis

1) Isotonic solutions: same osmotic pressure; solvent passes the membrane at the same rate both ways.
2) Hypotonic solution: lower osmotic pressure; solvent will leave this solution at a higher rate than it enters with.
3) Hypertonic solution: higher osmotic pressure; solvent will enter this solution at a higher rate than it leaves with.

Osmosis and Blood Cells

- Red blood cells have semipermeable membranes.
- If stored in a hypertonic solution, they will shrivel as water leaves the cell; this is called **crenation**.
- If stored in a hypotonic solution, they will grow until they burst; this is called **hemolysis**.
- Intravenous (IV) solutions **must** be isotonic to blood.


The arrows represent the net movement of water molecules.

Red blood cell in isotonic medium neither swells nor shrinks.

Crenation of red blood cell placed in hypertonic environment

Hemolysis of red blood cell placed in hypotonic environment

13.6 Colloids

- Suspensions of particles larger than individual ions or molecules, but too small to be settled out by gravity, are called **colloids**.
- Colloids form the dividing line between solutions and suspensions.

Table 13.5 Types of Colloids

Phase of Colloid	Dispersing (solvent-like) Substance	Dispersed (solute-like) Substance	Colloid Type	Example
Gas	Gas	Gas	-	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

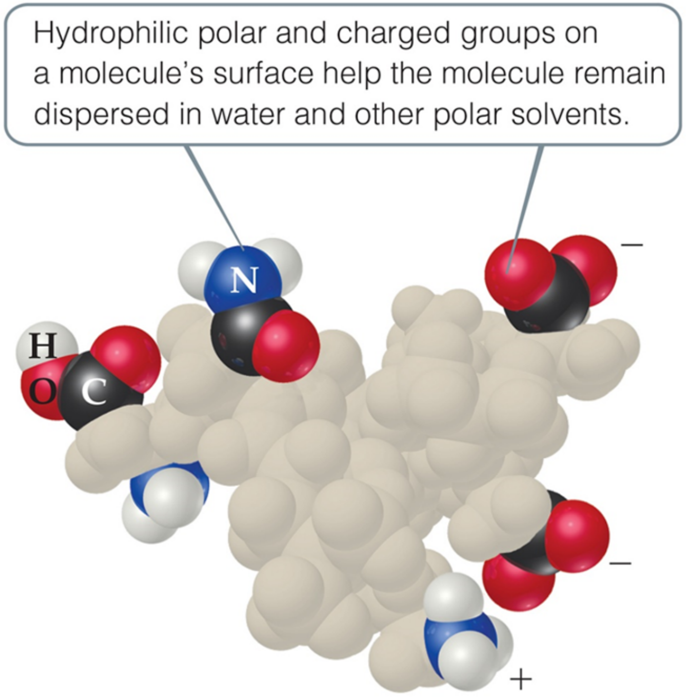
Tyndall Effect

- Brownian motion describes the solvent driven movement in colloids.
- Solutions do not scatter light. Colloidal suspensions can scatter rays of light.
- This phenomenon is known as the **Tyndall effect**.

The glass on the right holds a colloid. The one on the left holds a solution.

Colloids and Biomolecules

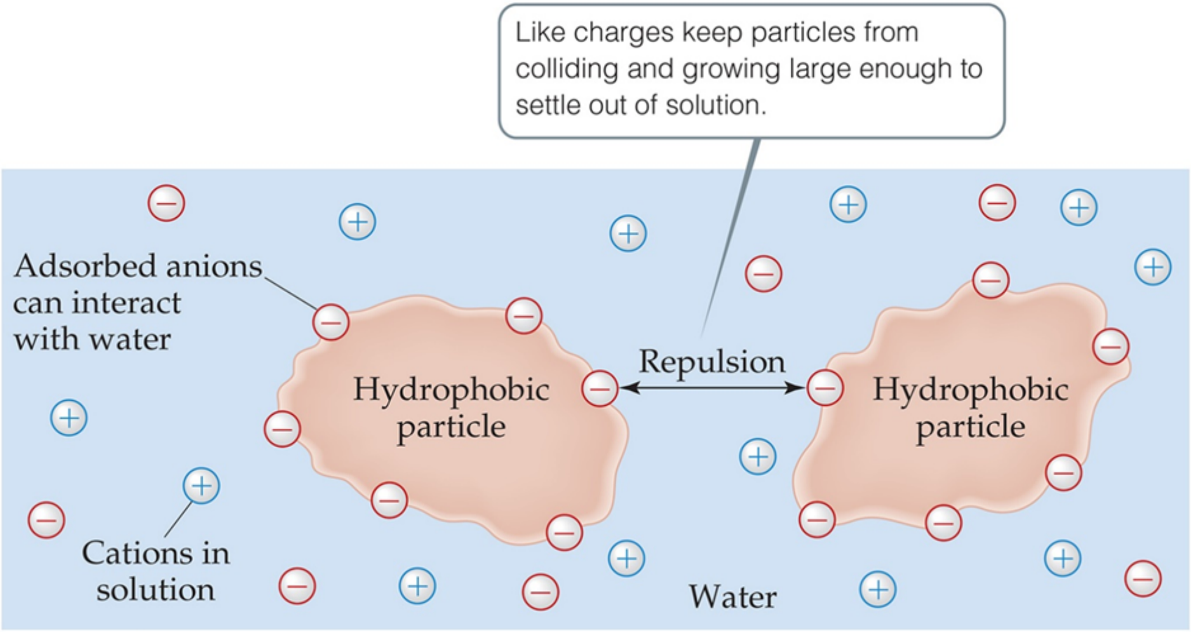
- Some molecules have polar, **hydrophilic (water-loving)** portions and nonpolar, **hydrophobic (water-fearing)** portions.
- Large molecules that form colloids in water often have the hydrophilic portions facing outward to interact with the water.



Hydrophilic polar and charged groups on a molecule's surface help the molecule remain dispersed in water and other polar solvents.

Stabilizing Colloids by Adsorption

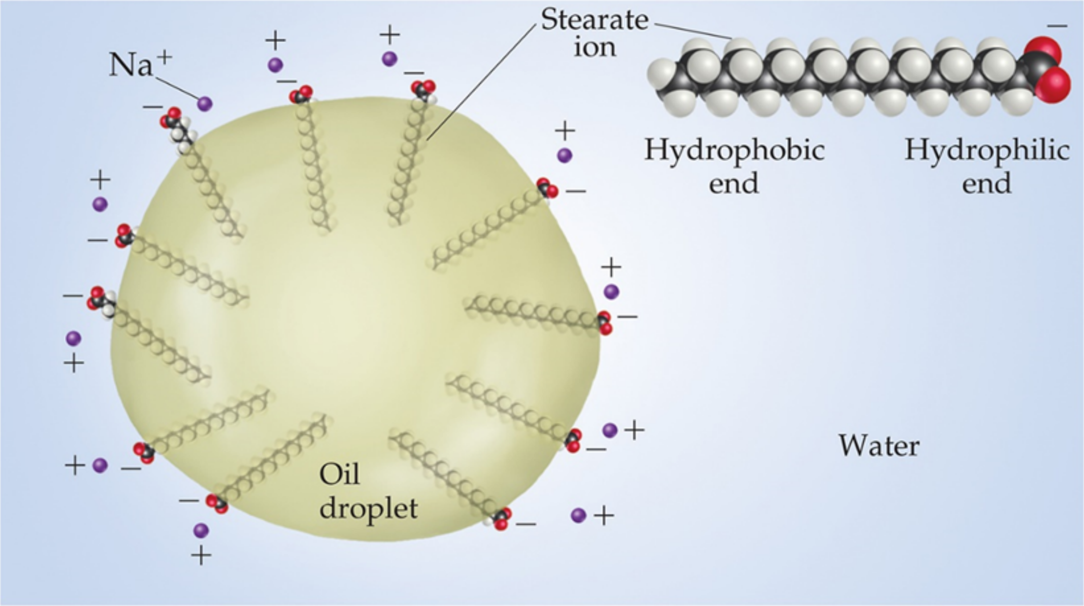
- Hydrophilic molecules often fold such that polar groups are on the surface where they can interact with water.
- Water adsorption at the surface stabilizes the colloid.



Like charges keep particles from colliding and growing large enough to settle out of solution.

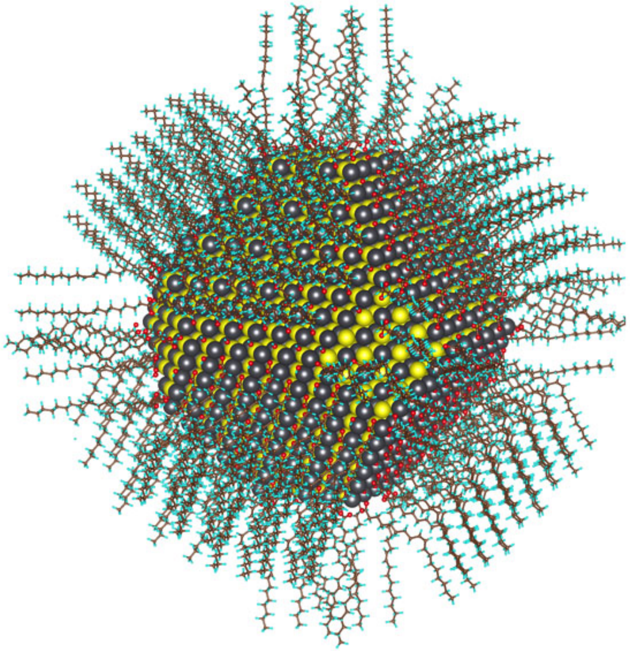
Colloids in Biological Systems

- Emulsifier molecules have nonpolar tails and polar heads.
- The hydrophobic tail imbeds into the hydrophobic molecule while the hydrophilic head interacts with the water solvent.
- This aides in digestion by allowing cell wall passage.



Colloids in Nanoscience

- Solid nanocrystals stabilized by surface ligands (Surfactants)

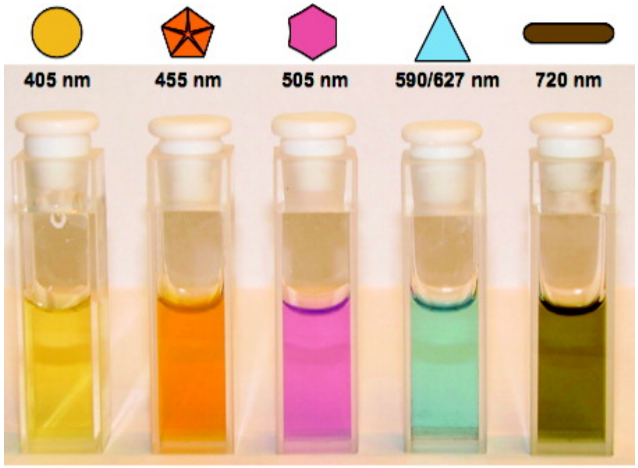


- Core: Metals (Au or Ag), Semiconductors (CdS, PbS, etc.)
- Surfactants: Amphophilic molecules, polymers, or DNA

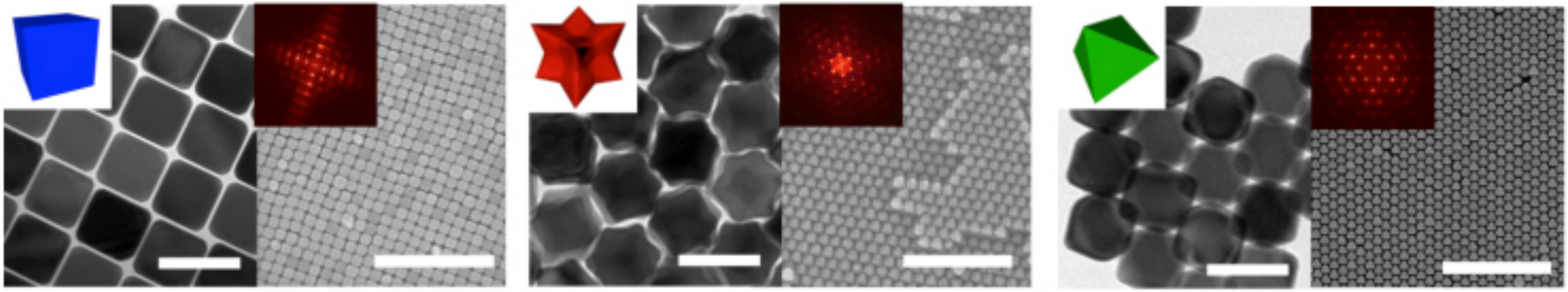
Colloidal metal nanocrystals

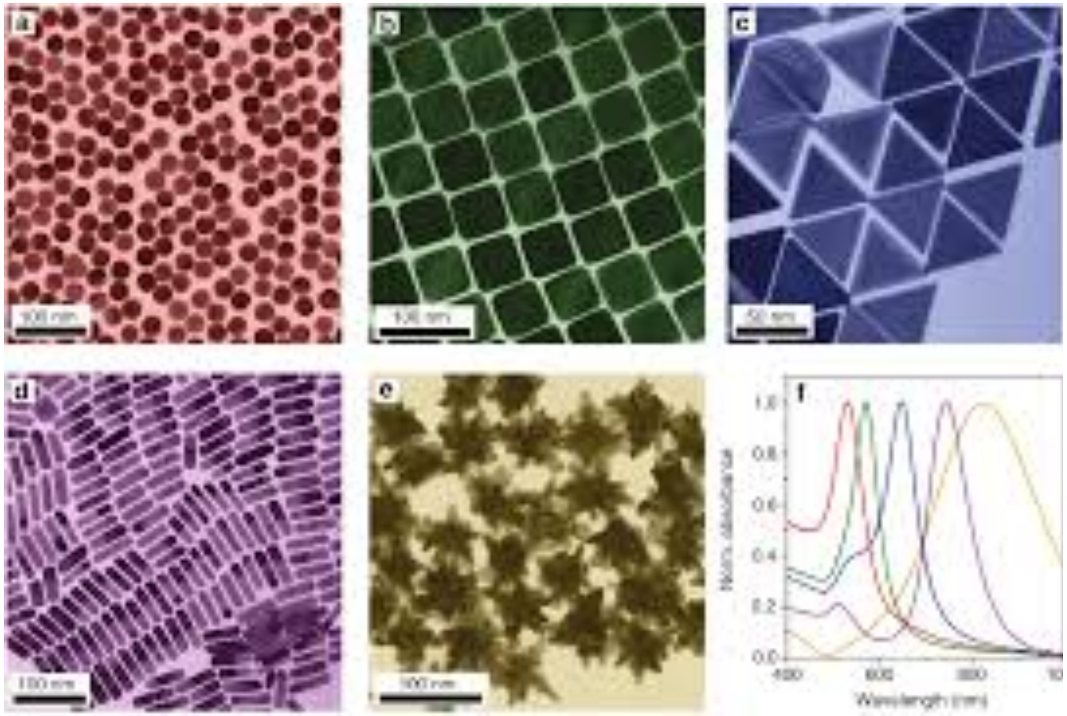
Size

Shape



Colloidal metal nanocrystals





Colloidal metal nanocrystals

- Lycurgus cup (from the AD 300’s)

Transmission

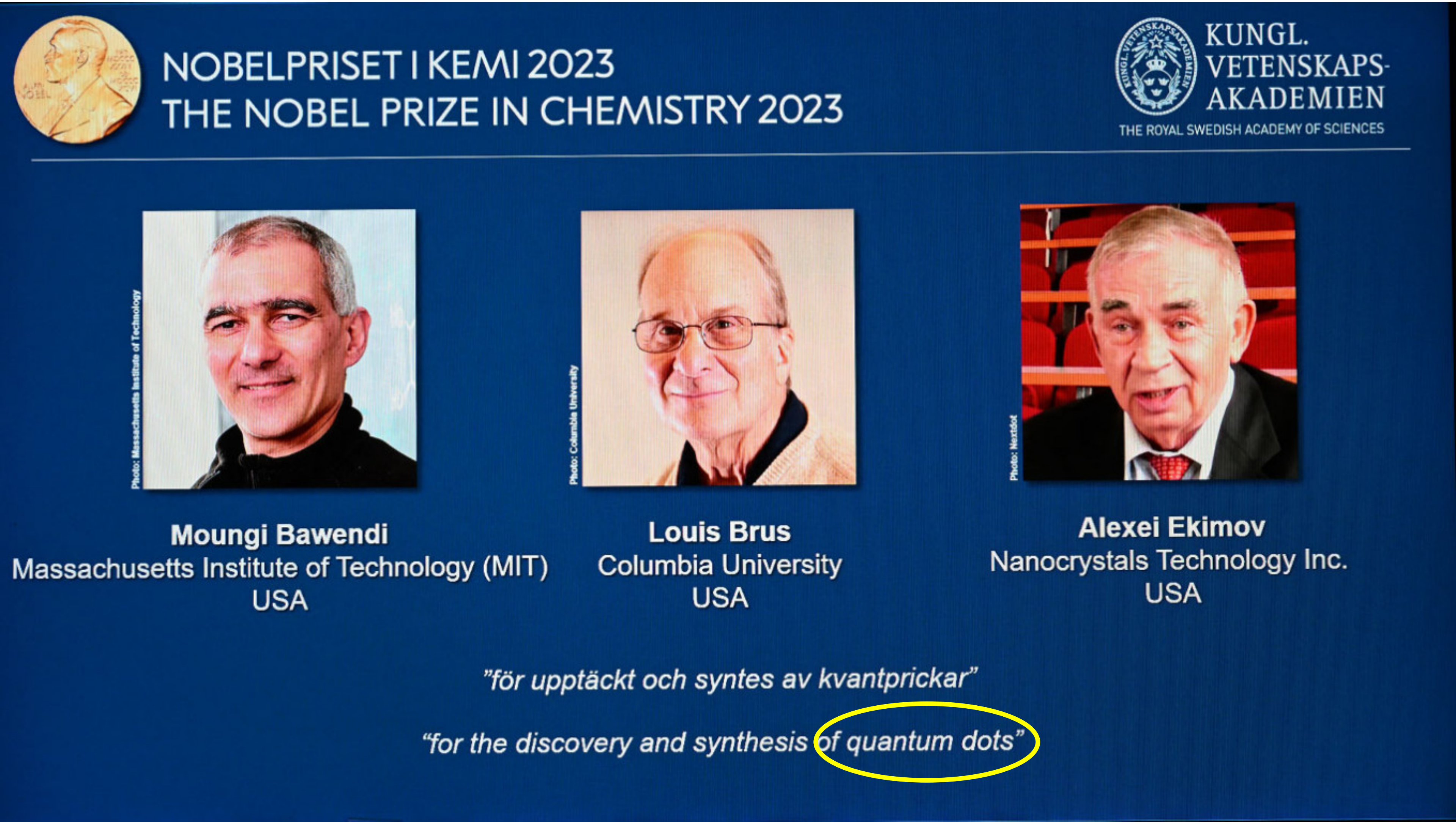
Reflection

Colloidal metal nanocrystals

- Stained glass

Colloidal semiconductor nanocrystals : “Quantum dots”

Colloidal semiconductor nanocrystals : “Quantum dots”



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THE NOBEL PRIZE IN CHEMISTRY 2023

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USA

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Louis Brus
Columbia University
USA

Photo: Nextdot

Alexei Ekimov
Nanocrystals Technology Inc.
USA

”för upptäckt och syntes av kvantprickar”

“for the discovery and synthesis of quantum dots”