

Chapter 15: Properties of “Solutions”

- homogeneous (uniform) mixture, usually liquid (also gas)

Q: Why does alcohol, salt, and sugar dissolve in water, but oil doesn't?

Facts

1. All gases mix fully
2. Only some liquids and solids “dissolve” in a given “solvent”
 - “solvent”: major liquid
 - “solute”: minor component dissolved
 - solids: “soluble” or “insoluble”
 - liquids: “miscible” or “immiscible”

15.1 Solubility and Noncovalent Forces

1. **Water** is strongly polar.

<u>Water Will Dissolve:</u>	<u>Strong Solvent-Solute Interaction</u>	<u>Examples</u>
a) many ionics	Ion-dipole	NaCl, KBr, LiNO ₃
b) H-bonders	Hydrogen-bonding	C ₃ H ₇ OH, C ₂ H ₅ NH ₂
c) molecules with N or O	Hydrogen-bonding	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$ $\begin{array}{c} \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{CH}_3 \\ \quad \\ \text{H}_2 \quad \text{H}_2 \end{array}$ $\begin{array}{c} \text{H}_2 \quad \text{H}_2 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{N}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$

- These groups are “hydrophilic”
- all end up with **strong solvent-solute** interactions in water
 - hydrogen-bonding or ion-dipole
 - the solute-water interactions may be similar, better, or not much worse than the original solute-solute and water-water interactions
- Q: How can “case c” molecules that have N or O hydrogen bond to water when they don't hydrogen-bond themselves?

<u>Water Won't Dissolve:</u>	<u>Solvent-Solute Interaction</u>	<u>Examples</u>
a) nonpolar molecules	Dipole-induced dipole	Br ₂ , N ₂ , SiH ₄
b) hydrocarbons, halocarbons	Dipole-induced/weak dipole	C ₆ H ₁₄ , C ₂ H ₅ Cl
c) weakly polar molecules without N or O	Dipole-weak dipole	PCl ₃ , SiHCl ₃

- These groups are “hydrophobic”
- all end up with **weak solvent-solute** interactions in water
 - none can hydrogen-bond with water
 - at best they end up with dipole (water)-weak dipole (solute), or dipole (water)-induced dipole (solute) interactions which are quite weak
 - the solute-water interactions are much inferior to water-water interactions. Therefore the energy penalty of breaking waters apart in order to allow solute into the water is prohibitively high.

☆ 2. **Adding C's to a molecule reduces polarity, reduces water solubility**

- adding more carbons is like adding more non-polar grease to a molecule

	C ₂ H ₅ OH	C ₃ H ₇ OH	C ₄ H ₉ OH	C ₅ H ₁₁ OH	C ₆ H ₁₃ OH	C ₇ H ₁₅ OH
Water Solubility:	Infinite	Infinite	9.1g/100mL	2.7g/100mL	0.6g/100mL	0.1g/100mL

☆ 3. **Hydrocarbons/Halocarbons are “Nonpolar”/”Weakly Polar”**

- Oils, grease, fat, gasoline
- Don't dissolve in water
 - Hydrocarbon-water interactions are too weak
- Dissolve weakly polar, nonpolar things
 - Interactions between solute-solvent may be weak, but not any weaker than the original solute-solute or solvent-solvent interactions

4. **“Like dissolves like” (general principle)**

	<u>Soluble?</u>
Hydrophilic-hydrophilic	Yes
Hydrophobic-hydrophobic	Yes
Hydrophilic-hydrophobic	No

- More alike, more soluble

Why?

- **Solute-solute interactions come at the expense of some solvent-solvent and solute-solute interactions**
 - To dissolve something in water, you need to separate water molecules from each other (at the expense of water-water hydrogen bonding) and also separate the solute molecules from each other (at the expense of solute-solute interactions)
- If the solute-solvent interactions are superior → good, soluble (H₂C=O in H₂O)
- If solute-solvent interactions are comparable → good, soluble (CH₃OH in H₂O or CH₄ in CH₂Cl₂)
- If the solute-solvent interactions are way worse → bad, insoluble (CH₄ in H₂O)

1) For each of the following substances, mark whether they would be more soluble in H₂O or C₆H₁₄.

<u>Substance</u>	H ₂ O	C ₆ H ₁₄
a. NH ₃		
b. Br ₂		
c. C ₁₂ H ₂₆		
d. CHCl ₃		
e. CH ₃ OCH ₃		

2) For each pair, circle the one that would be more soluble in water?

- a. CH_3NH_2 or CH_3Cl
 b. MgCl_2 or $\text{C}_6\text{H}_5\text{Cl}$
 c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{OH}$

3) Which is more soluble in CCl_4 ?

- a) C_6H_{10} or $\text{C}_3\text{H}_7\text{OH}$
 b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ or CH_3OH

15.2, 1 Enthalpy, Entropy, and Dissolving Solutes. The Solution Process

A. 2 Factors Influence spontaneity of any process

- Energy/enthalpy: Exothermic (good) or Endothermic (bad) or energy neutral
- “Entropy”: the order/disorder of a system
 - increasing disorder is natural
 - desk, office, brain, etc.
 - entropy/disorder increases \rightarrow favorable, spontaneous event
 - entropy/disorder decreases \rightarrow unfavorable, spontaneous event
 - work/energy is required to fight the natural tendency towards disorder
- If both enthalpy and entropy are in agreement, it's easy to decide whether a process will be favorable or not. If they disagree, you need to know which factor dominates.

B. Dissolving always increases entropy

- When a solute, which is originally organized together, dissolves and disperses throughout a solvent, the result is less order and more entropy

Solubility is primarily entropy-driven

Entropy always favors solubility

Q: When will something not dissolve?

A: Only if enthalpy is so bad (endothermic) that it overrules the entropy factor

4 Scenarios for dissolvings:

<u>Enthalpy</u>	<u>ΔH</u>	<u>Entropy</u>	<u>Will Dissolving Occur?</u>	<u>Why?</u>
1. Good	$\Delta H < 0$	Good	Yes	Entropy + Enthalphy
2. Indifferent	$\Delta H \sim 0$	Good	Yes	Entropy Driven
3. Slightly bad	$\Delta H > 0$, but only a little	Good	Yes	Entropy Driven
4. Very Bad	$\Delta H \gg 0$	Good	No	Enthalpy Driven

Point: Solubility fails only if strongly endothermic

- If exothermic, energy neutral, or only weakly endothermic, solubility succeeds
 - Endothermic dissolving is how ice fast packs work

C. Solubility Enthalpy



<u>Intermolecular Forces</u> Solute-solute interactions Solvent-solvent interactions		<u>Intermolecular Forces</u> Solute-solvent interactions
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Old interactions are traded for new solute-solvent interactions

- If the new are comparable or better than the old $\rightarrow \Delta H \leq 0$ (exothermic or neutral)
- If the new are weaker $\rightarrow \Delta H > 0$ (endothermic)

Only if the new solute-solvent interactions are substantially weaker than original interactions will ΔH be sufficiently endothermic to veto solubility

D. Why Like Dissolves Like

- in **like/like**, new solute/solvent IMF are similar to original
 - hydrophilic + hydrophilic: strong in, strong out (dissolving in water)
 - hydrophobic + hydrophobic: weak in, weak out (dissolving in nonpolar solvent)
 - $\Delta H \approx 0 \rightarrow$ soluble (**entropy gets it's way**)
- in **like/unlike case**, new solute/solvent IMF are much weaker than the original
 - hydrophilic (water) + hydrophobic (nonpolar): strong H-bonding in, weak dipole-induced dipole out
 - $\Delta H \gg 0 \rightarrow$ insoluble (**lousy enthalphy vetos entropy**)

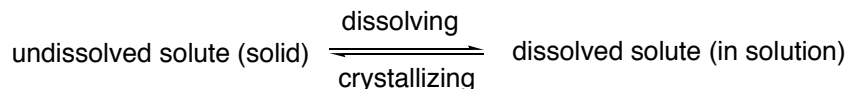
15.2 Solubility, Equilibrium, and Temperature (15.4)

- Solubility is quantified in grams of solute per 100 mL solvent
 - “Soluble”: defined as $>10\text{g}/100\text{mL}$
 - “Insoluble” does **not** mean that nothing can dissolve, or be important...
- Water can dissolve only so much solute, but not more...

3 Terms

1. “**unsaturated**” solution: the solvent could dissolve more solute.
2. “**saturated** solution”: the solvent has dissolved as much solute as it can hold
 - Caveat: as much as it can hold if it's *at equilibrium* (see supersaturation exception below)
 - Temperature: “saturation” is temperature dependent. At a higher temperature, a solvent will be able to dissolve more solute.
 - A saturated solution will normally have some undissolved solid sitting at the bottom.
3. “**supersaturated** solution”: the solvent has more dissolved solute than it can hold, if it were at equilibrium
 - A supersaturated solution is **not** at equilibrium.
 - If something happens to enable equilibrium to be reached, a bunch of solute will come out of the supersaturated solution.

Saturated Solution and Equilibrium: In a saturated solution, a dynamic equilibrium exists between dissolved and undissolved solute.



- Solid stuff is continuously dissolving into the solution
- But at the same time, dissolved solute is continuously crystallizing out of the solution.
- At dynamic equilibrium, the rates of dissolving and crystallizing cancel each other out
 - A steady state concentration of dissolved solute in the solution results
- Adding more solid makes no difference; the solvent can only hold so much solute.
 - Ex: Add 10g of X into 100mL water, but only 5g can dissolve. 5g stays undissolved.
 - Will adding another 10g of X get any more dissolved? No!
 - The pile of undissolved X just grows from 5g to 15g.
- Adding more solvent does make a difference.
 - Ex: Add 10g of X into 100mL water, but only 5g can dissolve. 5g stays undissolved.
 - Will adding another 100 mL of water get any more dissolved? Yes!
 - If the solubility is 5g X/100mL → 200 mL of water can dissolve all 10g of X.

Supersaturated Solution and Equilibrium: In a supersaturated solution, a dynamic equilibrium does **not** exist between dissolved and undissolved solute. (At least not yet.)

- All of the solute is dissolved, even though not that much would stay dissolved *if at equilibrium*
 - A supersaturated solution is never at equilibrium
 - There is no solid present
 - No crystallization occurs *as long as the solution remains supersaturated*
- If a seed crystal appears, by human addition or by spontaneous formation, then much crystallization occurs until equilibrium is reached
 - Crystallization requires a surface on which to form.

Solubility and Temperature (15.4):

Solids are more soluble at higher temperature

Temperature-based Crystallization: if a hot saturated solution is cooled → solubility decreased → crystals form

- Recrystallization of contaminated crystals: use a hot solvent to barely dissolve everything → cool back down → purified crystals form while contaminants remain dissolved in the solvent

Ionic Solutes in Water

1. “hydration”: when waters surround an ion and dissolves it
2. Old interaction: ionic bonds → new interaction: ion-dipole
 - The stronger the original ionic bonding, the less soluble (in general)
 - Normally +1 and -1 ions hydrate well, and dissolve best.
 - +2 and +3 cations tend to lead to less water soluble salts.

High Water Solubility

LiCl, NaBr, KNO₃

Low Water Solubility

CaSO₄, Ba₃S₂, Mg₃(PO₄)₂

15.7 Impact of Solute on 3 Properties of Solutions

- Solutes alter properties that involve phase changes
- Dissolved solute essentially dilutes the solvent
- The molar quantity of dissolved particles is what matters
- “Molality” = moles solute particles/kg of solvent

1. **Vapor Pressure** is Reduced

- If solution is only 95% solvent → vapor pressure will be only 95% of normal

2. **Boiling Point** is Elevated

- Salt raises the boiling point of water
- Increased molality → reduced vapor pressure (solvent escape rate) → temperature needs to rise to reach the boiling point
 - (since vapor pressure must equal external pressure at boiling point...)

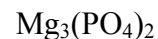
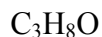
3. **Freezing Point/Melting Point** is Depressed

- Why we put salt on ice (CaCl_2 usually)
- Why does it happen?
 - As solvent is diluted, fewer are able to crystallize, so freezing slows down, and you need to get colder to force it
- Freezing range is not only lowered, but is also greatly broadened
- Ice freezes as pure water, so the remaining water gets more and more concentrated in salt, resulting in further depression, etc..
- Note: pressure also reduces melting point
 - At many temperatures, ice skates melt the ice and the thin film of water makes the skates go faster

Key: Impact on melting point, boiling point, and vapor pressure depends on **moles of particles**

- One mole of an ionic substance produces more than one mole of particles

Q1: For the following, how many moles of solute particles are produced when 1 mole of “formula” is dissolved? If one mole of each is placed into a liter of water, rank them in terms of how much they would depress the boiling point.



Moles:

Rank:

Q2: Which would depress more, adding 1 mole of CH_3OH or 0.5 moles of $\text{Al}(\text{NO}_3)_3$?

Q3: If adding 1 mole of CH_3OH caused a 12° depression, how much depression would occur upon adding 0.5 moles of $\text{Al}(\text{NO}_3)_3$?

Q4: Which would cause more depression, adding 13 g of LiF (26 g/mol) or 90g of $\text{C}_6\text{H}_{12}\text{O}_6$ (180 g/mol)?

15.8 Osmosis: Selective Movement of Solvent Through a Semipermeable Membrane

- Membrane is selective: only some things (usually solvent) can pass through
 - Like a sieve or a filter
 - Usually based on size (water is small)
 - Cell walls
- Movement is motivated (usually) by a desire to equalize concentrations
- **Normally solvent moves from the “dilute” to the “concentrated side”**
 - This makes the dilute side more concentrated, and the concentrated side more dilute, until ideally they eventually meet in the middle

Volume of “concentrated” side grows (as more solvent comes over) Volume of “dilute” side shrinks (as solvent leaves)

Cells have modest salt concentration, and undergo osmosis through cell walls

1. Placed in concentrated salt solution (“hypertonic”), cell passes water out, shrinks, dehydrates
2. Placed in pure water (“hypotonic”), cell passes water in, swells, and bursts
 - “lyse” a cell for biology purposes
 - impact on “hydrating” a dehydrate person: just water will burst the cells

Other Osmosis Trivia

- Pickles: Cucumber shrinks in high salt
- Salt/sugar meats/fruits: bacteria get dehydrated and die → preserves “dried” meat
- H_2O transport in plants: absorb water from soil
- Diabetes: bad metabolism → high concentrations of solutes → need water, high thirst
- Edema: salty food → water retention → puffiness