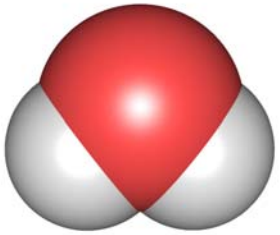
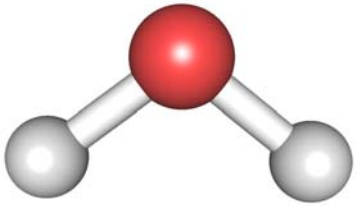
H_2O



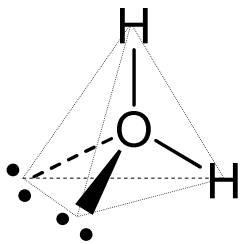


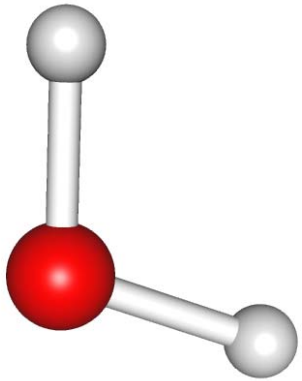
The chemical composition of a bacterial cell

	% of total cell weight	# of types of molecules
Water	70	1
Inorganic ions	1	20
Sugars and precursors	3	200
Amino acids and precursors	0.4	100
Nucleotides and precursors	0.4	200
Lipids and precursors	2	50
Other small molecules	0.2	200
Macromolecules (proteins, nuc. Acids, polysaccharides, etc.)	22	5000

Molecular properties of water

- sp^3 hybridized O, two lone pairs, tetrahedral e^- pair geometry, bent molecular geometry, polar, dipole moment





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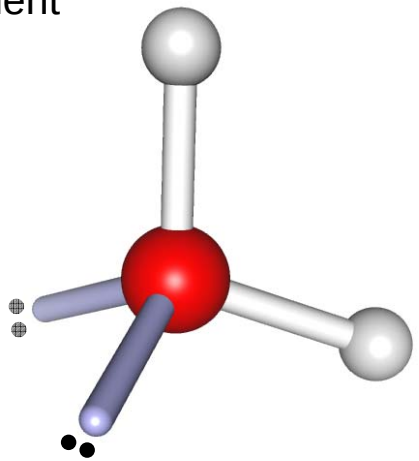

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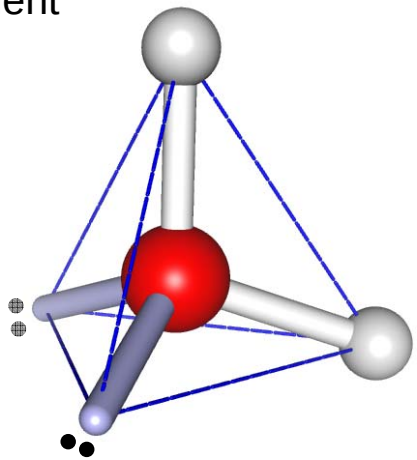

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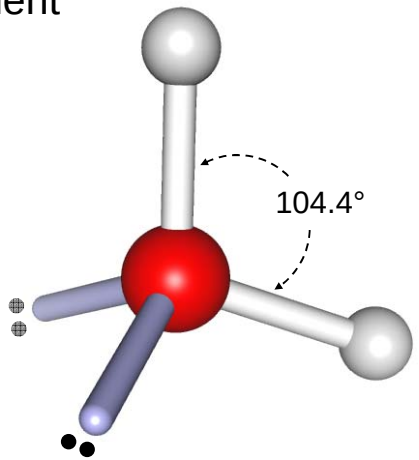

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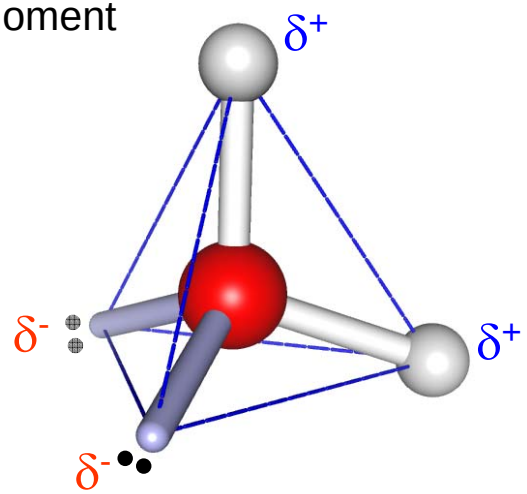

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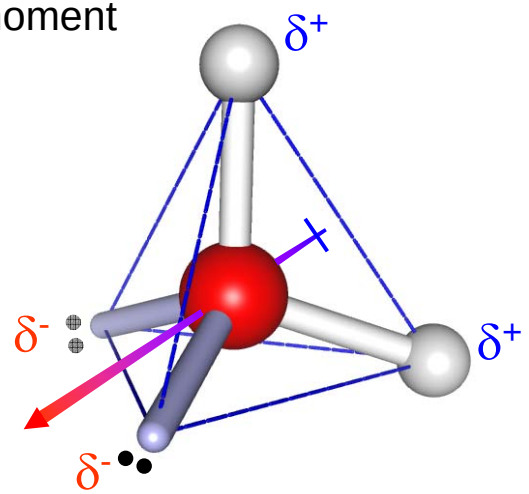

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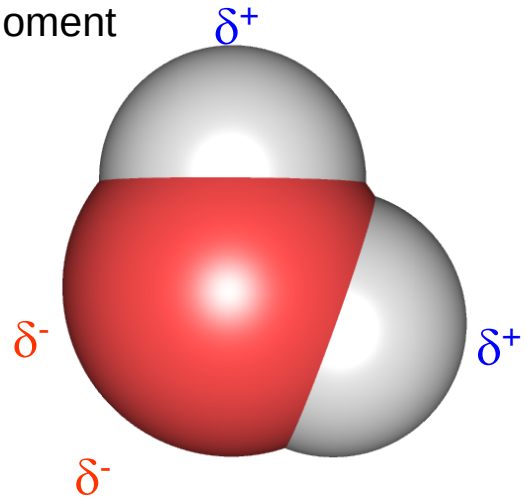

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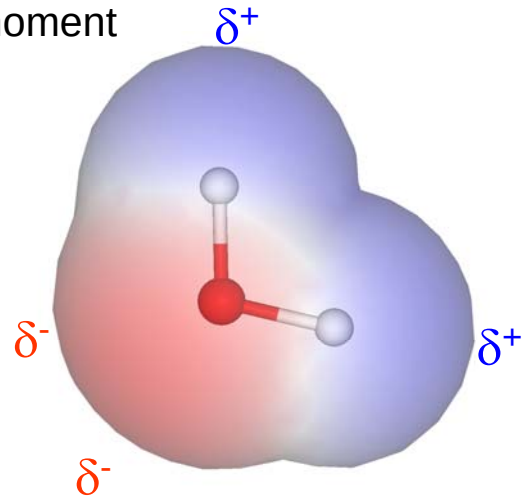
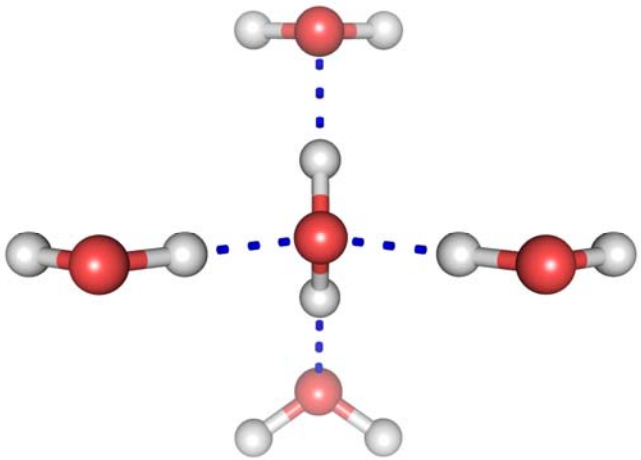


Why an aqueous environment?

The unique properties of H_2O stem from H-bonding:



Review of attractive forces

- intramolecular forces: atoms within molecules: ~150-1000 kJ/mol
  - molecular compounds: covalent bonds (bond energies)
  - ionic compounds Ion bonds (lattice energies)
- intermolecular forces: between separate molecules or ions: 0.05 – 25 kJ/mol
  - dipole-dipole
  - London dispersion (van der waal)
  - H-bonding
  - ion-dipole

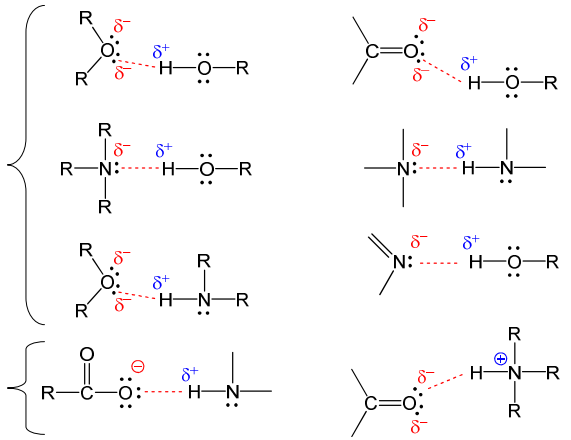
Review of intermolecular forces

Hydrogen bonds

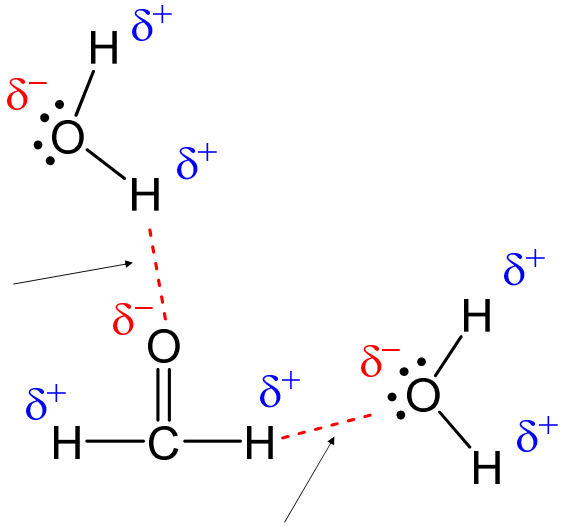
- Hydrogen acceptor: a lone pair on N, H, or O
- Hydrogen donor: a hydrogen that is bonded to N, O, or F
- Examples:

H-bonds involving neutral molecules

H-bonds involving an ion



Formaldehyde in water

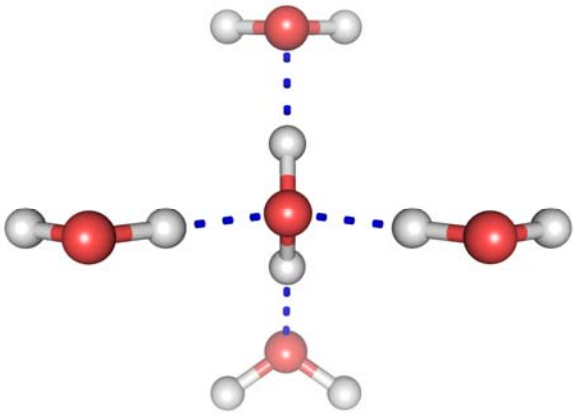


Some biologically important hydrogen bonds involving H_2O

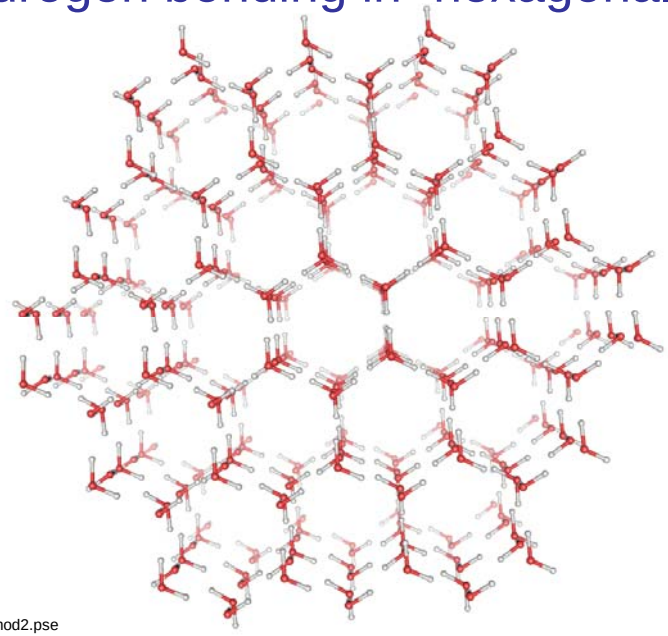
- alcohols, amines, amides, aldehydes, ketones, imines, carboxylic acids, esters, etc.

Hydrogen bonding in solid water

- Ordered three-dimensional crystalline network
- Each water H-bonded to four other molecules
- “Hexagonal” structure

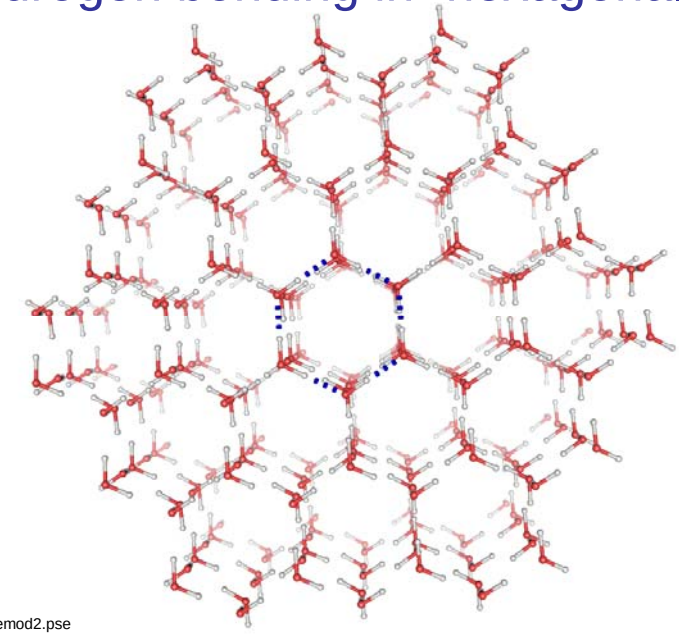


Hydrogen bonding in “hexagonal ice”



ICES-hex saemod2.pse

Hydrogen bonding in “hexagonal ice”



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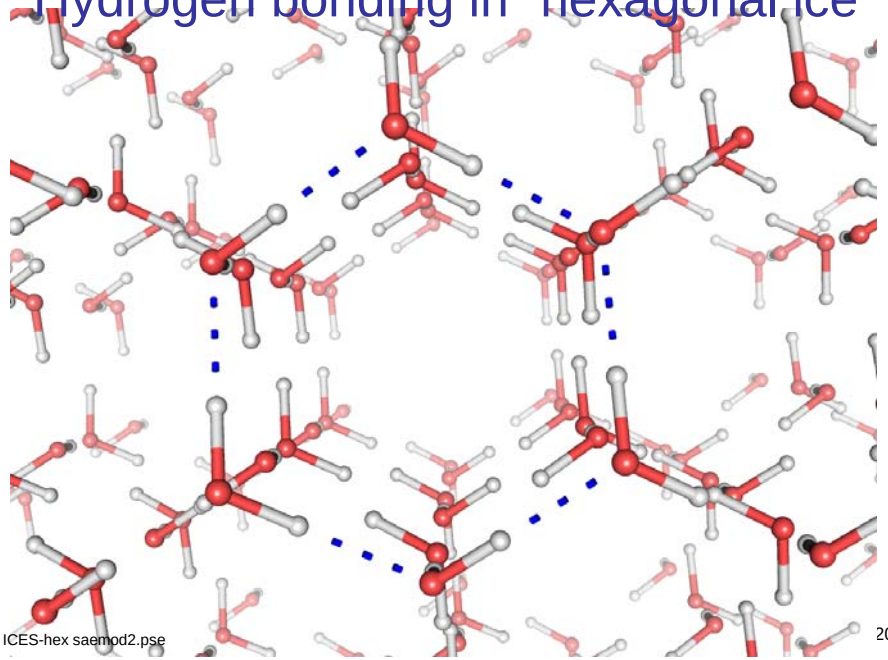

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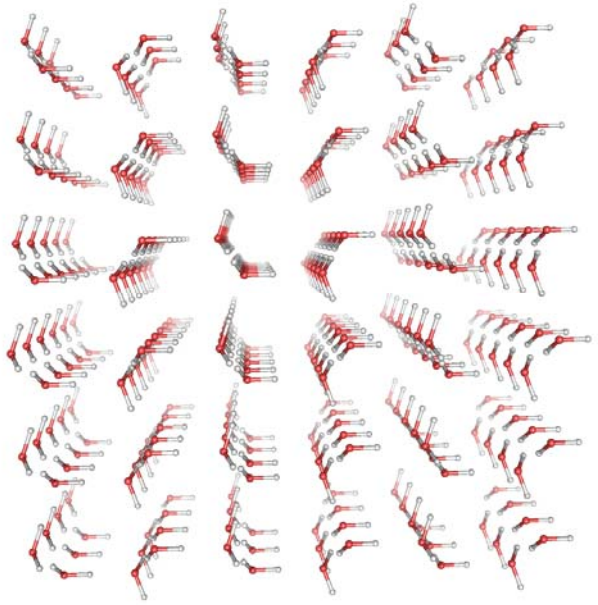
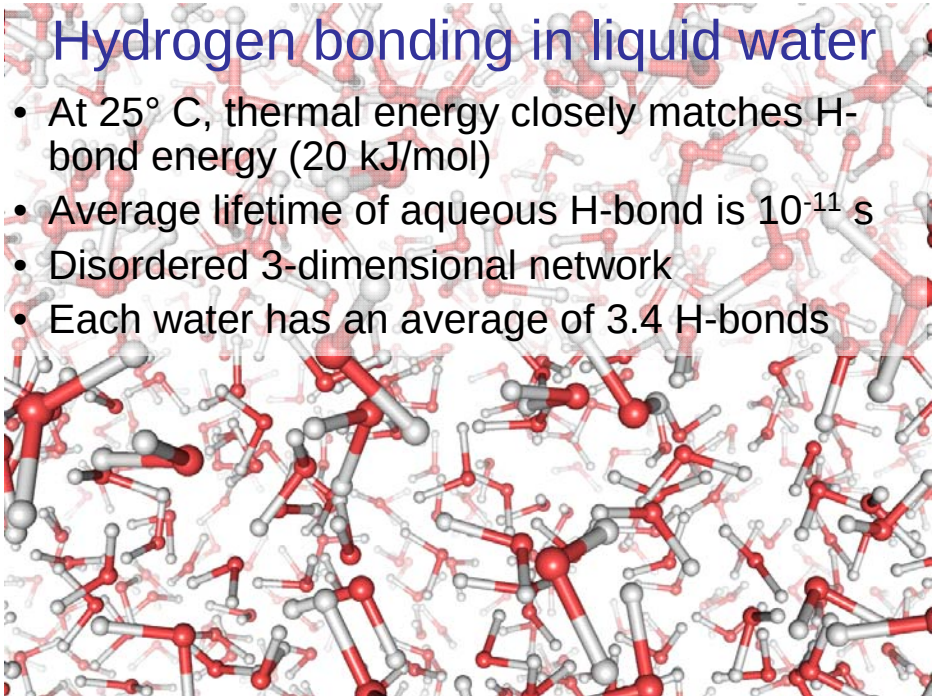


ICES-hex saemod2.pse

Hydrogen bonding in liquid water

- At 25° C, thermal energy closely matches H-bond energy (20 kJ/mol)
- Average lifetime of aqueous H-bond is 10^{-11} s
- Disordered 3-dimensional network
- Each water has an average of 3.4 H-bonds



The unique properties of H_2O stem from H-bonding

- $Density_{ice} < density_{liquid}$
- High heat capacity
- High ΔH_{vap}
- Interactions with biological molecules
  - *Dictates the folding and function of biological macromolecules*
- Autoionization

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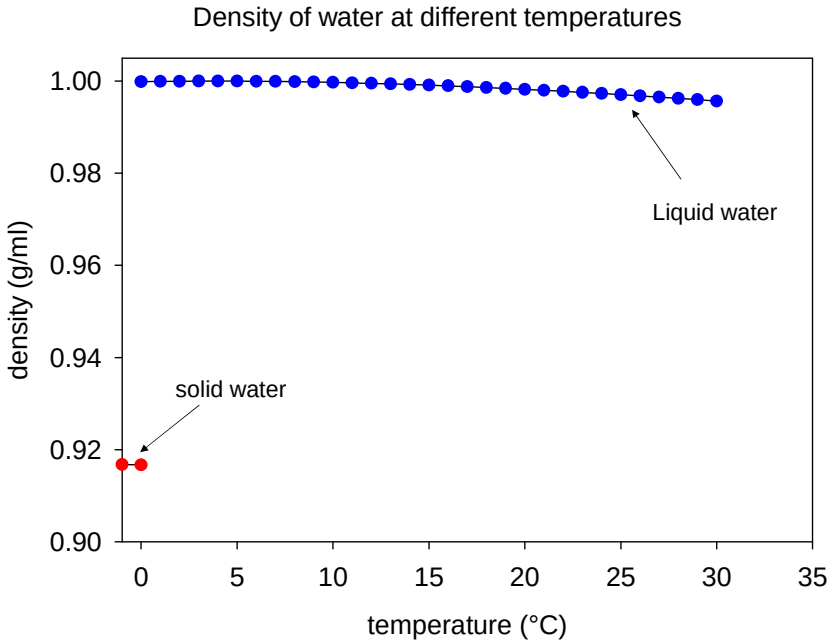
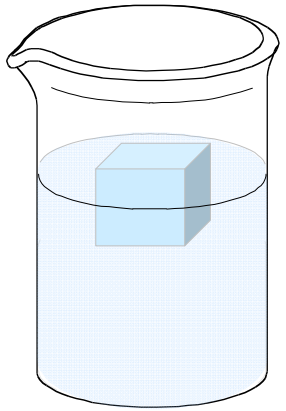
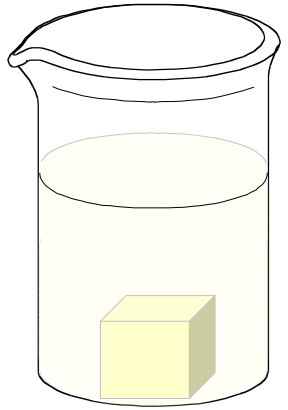


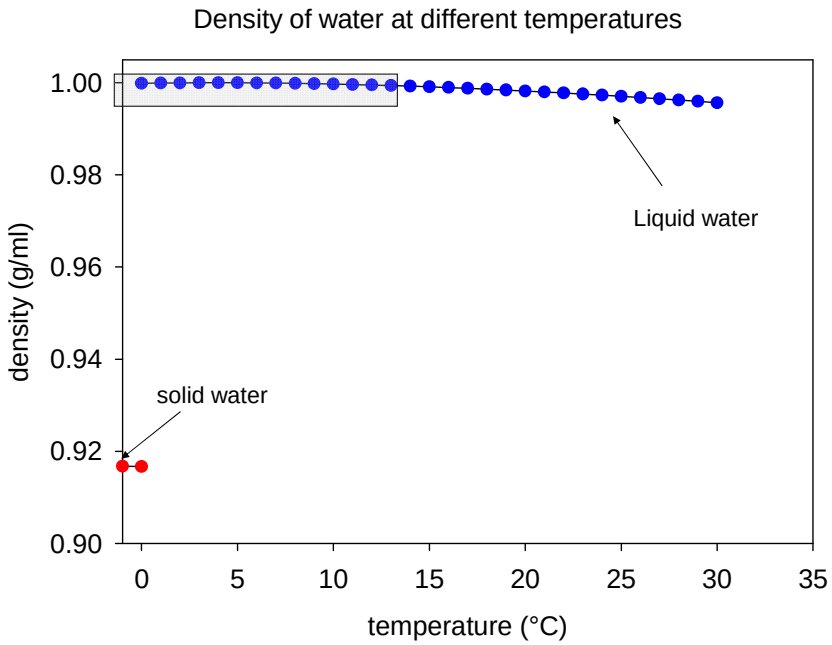
Water is the only nonmetallic compound for which the solid is less dense than the liquid



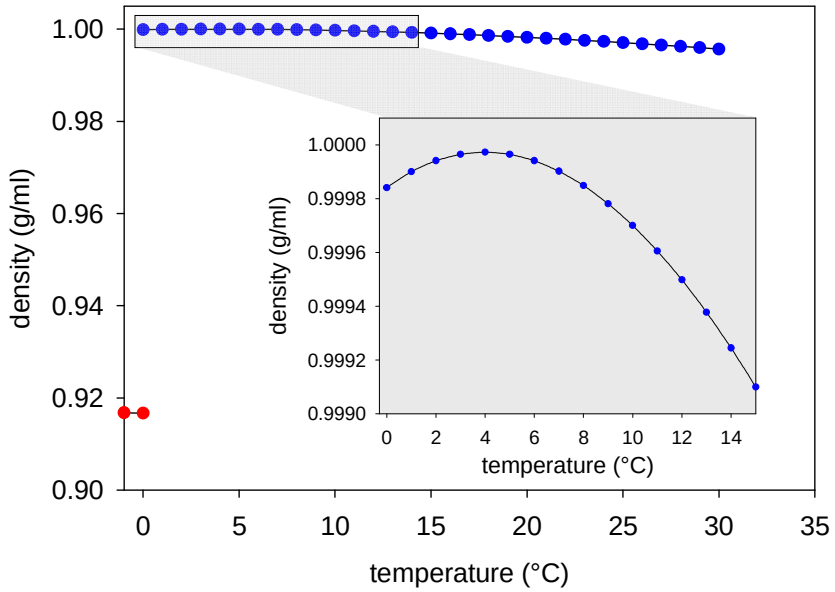
water



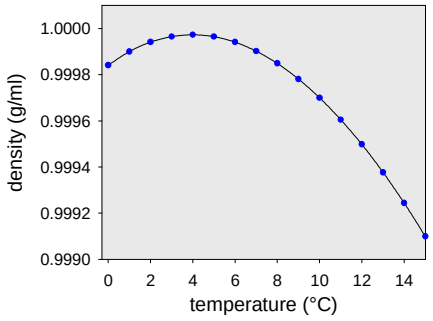
All other molecular compounds

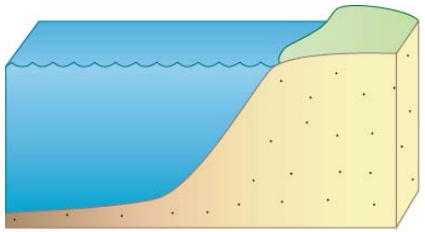


Density of water at different temperatures



Consequences of water having a maximal density at 4° for lake stratification and turnover





The unique properties of H_2O stem from H-bonding

- High heat capacity
  - Specific heat H_2O = 4.18 J/g/°C
  - Water is a "heat buffer": a large amount of heat can be absorbed with relatively little change in temperature

The unique properties of H_2O stem from H-bonding

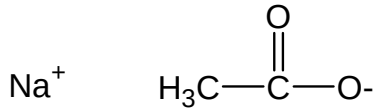
- High ΔH_{vap} (2.24 kJ/mol)
  - A large amount of heat is required to change water from a liquid to a gas
  - Biological exploitation in "evaporative cooling"

The unique properties of H_2O stem from H-bonding

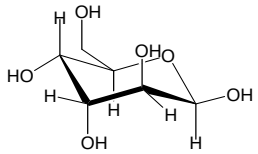
- Interactions with biologically relevant molecules
  - – Low molecular weight compounds
    - Ions
    - Polar molecules
    - Nonpolar molecules
    - Amphipathic molecules/ions
  - – Macromolecules
    - Proteins
    - Polysaccharides
    - Lipids
    - Nucleic acids

Potential solutes in water

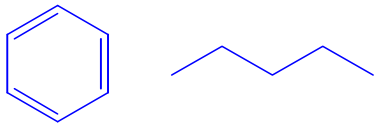
1. Ions



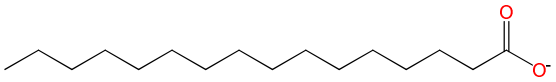
2. Polar molecules



3. Nonpolar molecules



4. Amphipathic molecules/ions



Polar and ionic solutes interact favorably with water due to H-bonding, dipole-dipole, and/or ion-dipole interactions

Fate of potential solutes in water

Do they dissolve? To what degree?

Consider:

- Solute-solute interactions (disrupt)
  - applies to solids and liquids but not gases, since there are no intermolecular attractive forces present in gases
- Solvent-solvent interactions (disrupt)
- Solute-solvent interactions (form)
- $\Delta G = \Delta H - T\Delta S$

Consider the solution process for a polar, molecular solid (e.g. glucose)

1. Break intermolecular attractions in solid glucose to free up individual molecules

   $(glucose)_n \rightarrow n\ glucose$

2. Disrupt water-water intermolecular attractions to provide room for glucose to dissolve

   $(water)_m \rightarrow m\ water$

3. Form new glucose-water intermolecular forces

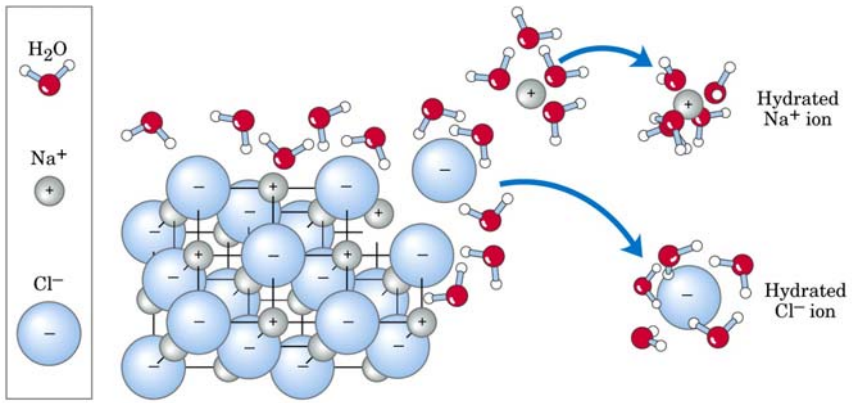
   $n\ glucose + m\ H_2O \rightarrow (glucose)_n(water)_m$

Do they dissolve? To what degree?

Consider:

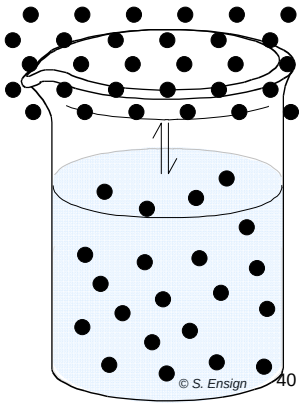
	ΔH ?	ΔS ?
• Solute-solute interactions (disrupt) $(glucose)_n \rightarrow n\ glucose$		
• Solvent-solvent interactions (disrupt) $(water)_m \rightarrow m\ water$		
• Solute-solvent interactions (form) $n\ glucose + m\ H_2O \rightarrow (glucose)_n(water)_m$		
• $\Delta G = \Delta H - T\Delta S$		

Solvation of an ionic or polar solute can be entropically and/or enthalpically driven



Solubility of gases in water

- No initial intermolecular attractive forces need to be broken
- Nonpolar gases: London attractive forces to water (poorly soluble)
- Polar gases: additional attractive forces (more soluble)



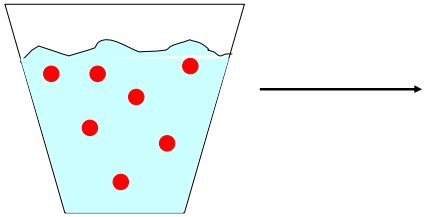
Solubility data for some gases in water at 298 K

Molecule	Mr	structure	Predominant intermolecular attraction with water	Solubility (g solute/kg H_2O)
H_2	2.02	H—H	London	0.0015
CH_4	16.1		London	0.021
N_2	28		London	0.018
O_2	32		London	0.039
CO_2	44		London	1.5
H_2S			Dipole-dipole	3.3
SO_2			Dipole-dipole and hydrogen bonding	94
NH_3			Hydrogen bonding	470

Solvation of a nonpolar molecule?

The hydrophobic effect

- Suppose that you add individual molecules of a nonpolar solute (e.g. hexane) to water. What happens?



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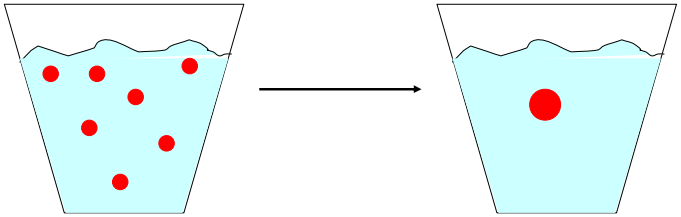

- Why does hexane aggregate?

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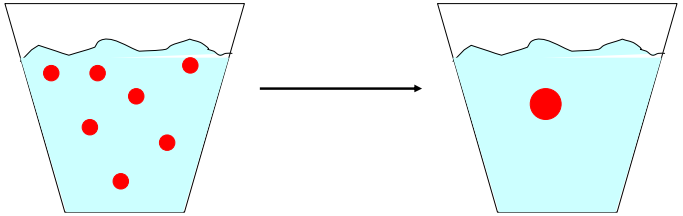

- Why does hexane aggregate?
  - Affinity of solute molecules for one another ? (ΔH)

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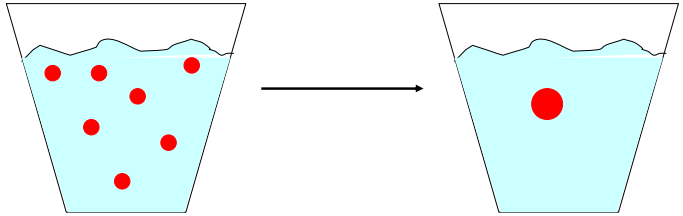

- Why does hexane aggregate?
  - Affinity of solute molecules for one another ? (ΔH)

Not the primary driving force, because the weak attractive van der waals forces may not significantly overcome the decrease in entropy imposed by association

The hydrophobic effect

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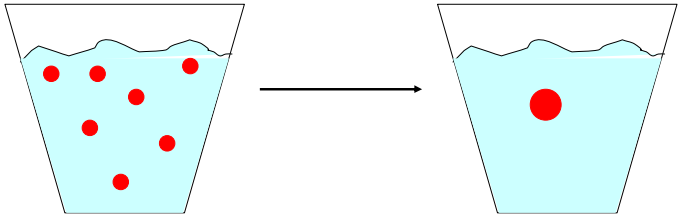

- Why does hexane aggregate?
  - Increase in entropy from disordering ordered water cages is the driving force (ΔS)

The hydrophobic effect

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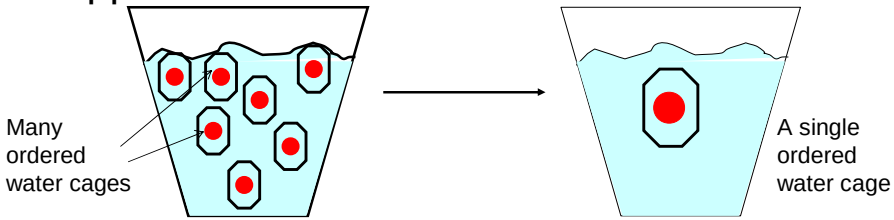
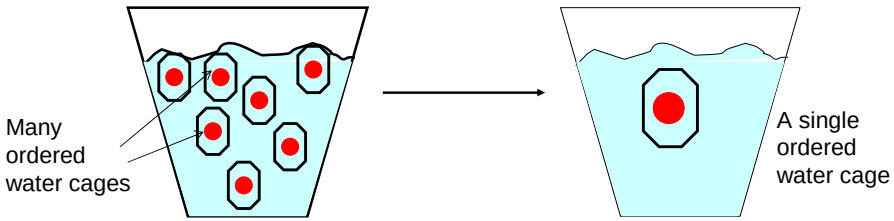
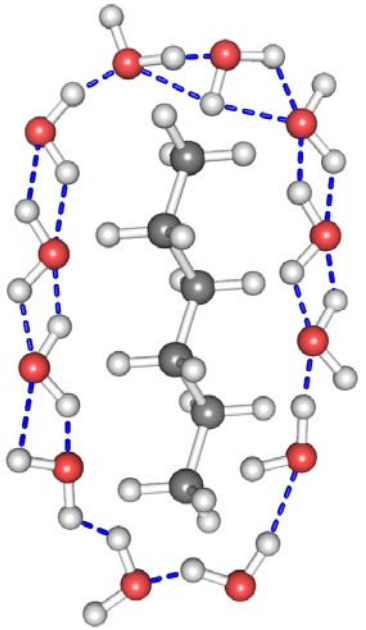


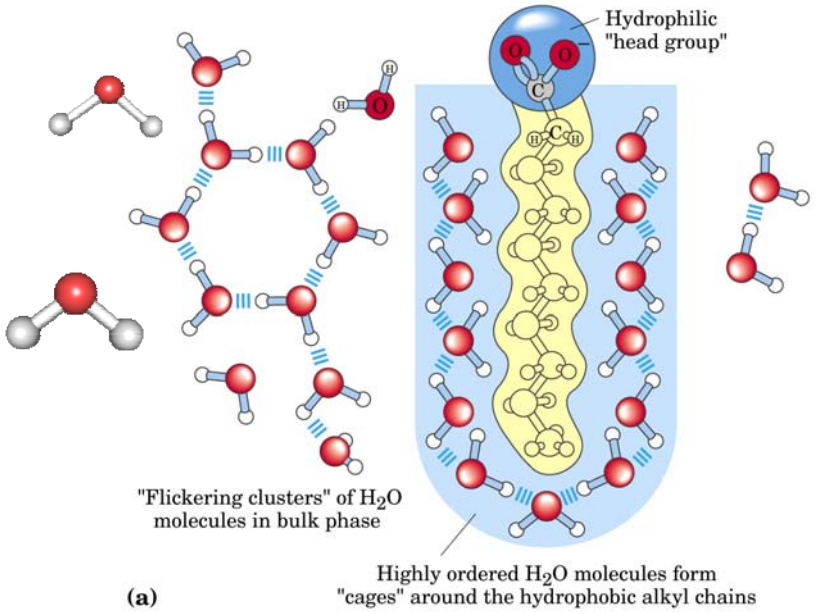
- Why does hexane aggregate?
  - Increase in entropy from disordering ordered water cages is the driving force (ΔS)

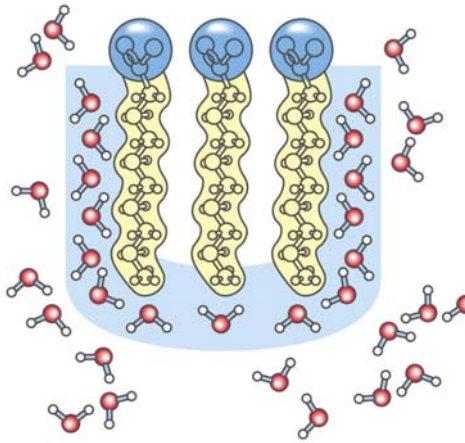
The hydrophobic effect

- The randomness gained by the release of higly ordered bound water molecules far exceeds the order imposed by the association of solutes







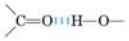
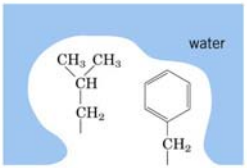


Clusters of lipid molecules

Only lipid portions at the edge of the cluster force the ordering of water. Fewer H_2O molecules are ordered, and entropy is increased.

table 4–4

Four Types of Noncovalent ("Weak") Interactions among Biomolecules in Aqueous Solvent

Hydrogen bonds	
Between neutral groups	
Between peptide bonds	
Ionic interactions	
Attraction	
Repulsion	
Hydrophobic interactions	
Van der Waals interactions	Any two atoms in close proximity

Why an aqueous environment?

The unique properties of H_2O stem from H-bonding:

- High heat capacity
- High melting and boiling points
- High ΔH_{vap}
- $Density_{ice} < density_{liquid}$
- Interactions with biological molecules
  - ➢ *Dictates the folding and function of biological macromolecules, largely due to the hydrophobic effect*

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- Ionization of water

Ionization of water

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

The “proton” in solution

Acids and bases

- Lewis acid/base: electron pair acceptor/donor
- Arrhenius acid/base: dissolves in water to increase/decrease $[H^+]$
- Brønsted-Lowry acid/base: proton donor/acceptor

Acid and base definitions

- Arrhenius acid: a substance that dissolves in water, increasing $[H^+]$
- Arrhenius base: a substance that dissolves in water, increasing $[OH^-]$
- Brønsted-Lowry acid: a proton donor
- Brønsted-Lowry base: a proton acceptor
- Lewis acid: an electron pair acceptor
- Lewis base: an electron pair donor

Ionization of weak acids and bases

- conjugate acid/base pairs

Ionization of weak acids in water

$HA \rightleftharpoons H^+ + :A^-$ $\qquad K_a = \dfrac{[H^+]\cdot[A^-]}{[HA]}$

$HA + H_2O \rightleftharpoons H_3O^+ + :A^-$ $\qquad K_a = \dfrac{[H_3O^+]\cdot[A^-]}{[HA]}$

$$pH = -\log[H_3O^+] = -\log[H^+]$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Ionization of weak bases

$B: + H_2O \rightleftharpoons BH^+ + OH^-$

- base dissociation constant: $K_b = \dfrac{[BH^+]\cdot[OH^-]}{[B]}$

- Examples of weak bases?

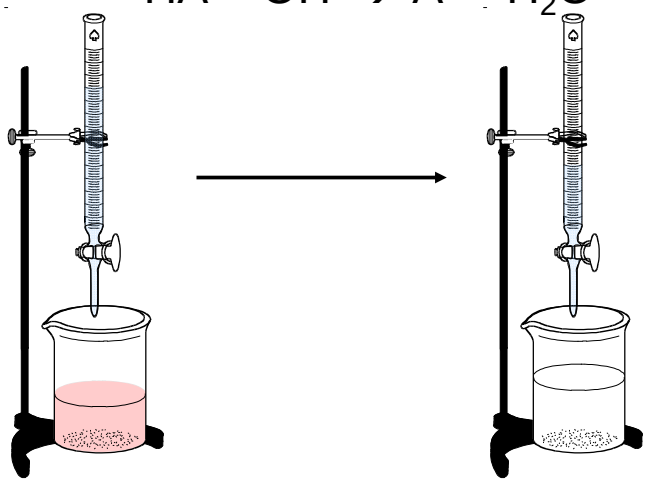
$$K_a \cdot K_b = K_w$$

Henderson-Hesselbach Equation

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Titration of a weak acid with a strong base

$HA + OH^- \rightarrow A^- + H_2O$

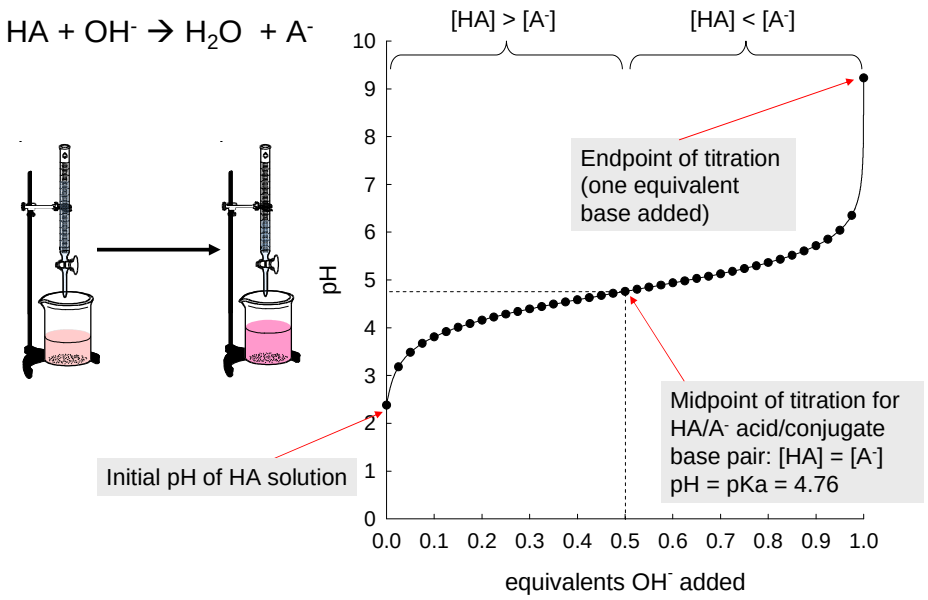


Solution of weak acid before base is added

Solution after "one equivalent" of strong base is added

Titration curve for a weak acid with a strong base: 1.0 M acetic acid titrated with 1.0 M NaOH

$HA + OH^- \rightarrow H_2O + A^-$



Significance of the numerical values of K_a and pK_a for a weak acid

- K_a:
  - the larger the K_a value, the stronger the acid
  - K_a values for weak acids will have values significantly less than one (~10^{-2} to 10^{-10}).
- pK_a:
  - the lower the pK_a value, the stronger the acid
  - pK_a values will be positive numbers (2 and 10 for examples above)
  - the value of pK_a tells you the pH at which the concentrations of HA and A^- will be equal in a solution containing both HA and A^-

Buffer solutions

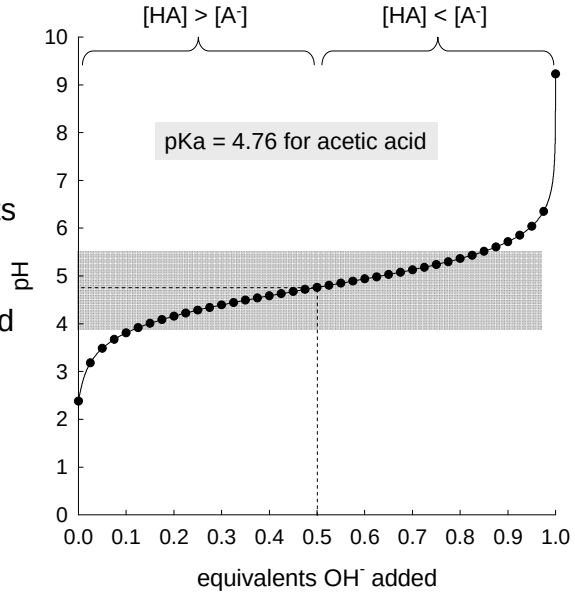
- Solutions containing a weak acid and it's conjugate base (or a weak base and it's conjugate acid) (HA & A^- or BH^+ & B)
- Buffer solutions resist change in pH upon addition of either acid or base, hence the name "buffer" ("resist change")
  - Add some acid to the buffer:
  - Add some base to the buffer:

Under what conditions does a buffer work best?

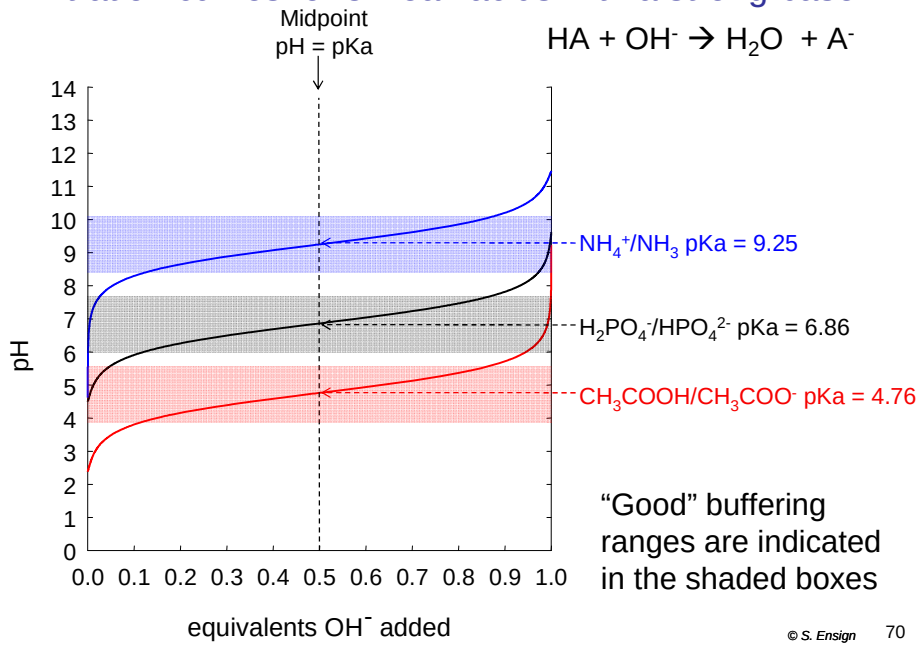
- Resist pH change in both directions
- $[HA] = [A^-]$
- When $[HA] = [A^-]$, $[H^+]$ = the numerical value of K_a for the weak acid
- $pK_a = -\log K_a$
- Select a buffer whose acid form has a pK_a close to the pH value you want to maintain

The region of “good” buffering capacity is shown in the shaded box

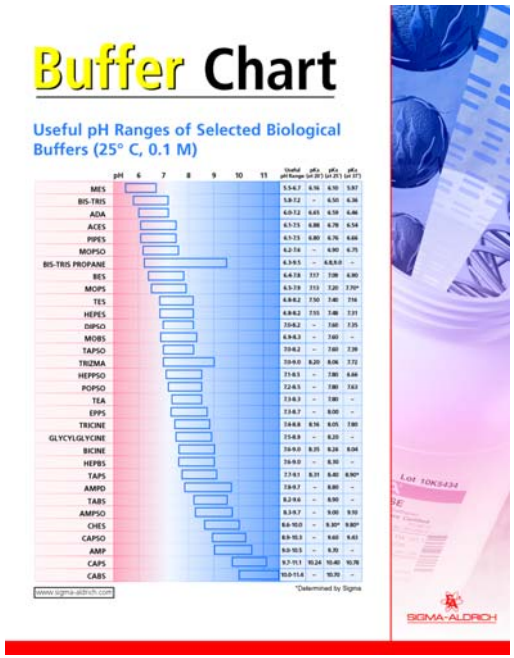
- A good rule to follow: select a buffer with a pKa that has a value within 0.5-1 pH units of the pH you want to maintain (this is the region with good buffering capacity)
- Acetic acid is a “good” buffer between pH values of ~4 and 5.5 (shaded region)



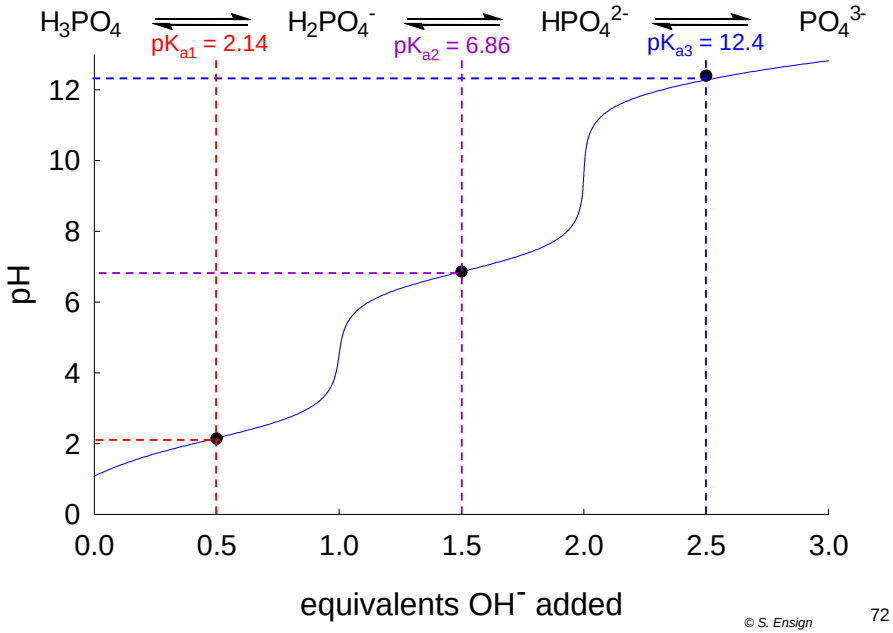
Titration curves for 3 weak acids with a strong base



“Good” buffering ranges are indicated in the shaded boxes



Polyprotic acids have more than one ionizable group



Biochemists work buffer problems, such as…

- Calculate the pH of a solution with known concentrations of HA and A^-
- Determine the masses of HA and A^- (as neutral acids, bases, or their salts) that must be dissolved in a given volume of solution to obtain a buffer solution with a desired pH
- Calculate the pH of a buffer solution after addition of some volume of acid or base
- Determine concentrations of HA and A^- in a buffer solution given total concentration of buffer species ($HA + A^-$) and pH