

Chapter 2 - Water

Water exists as a H-bonded network with an average of 4 H-bonds per molecule in ice and 3.4 in liquid.

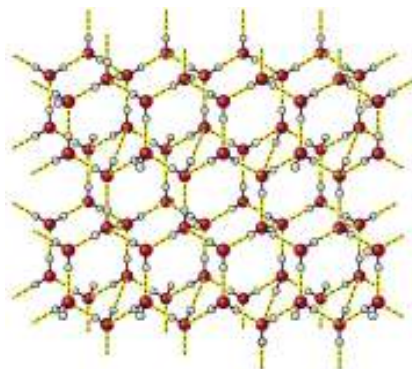


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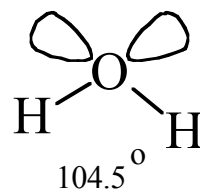
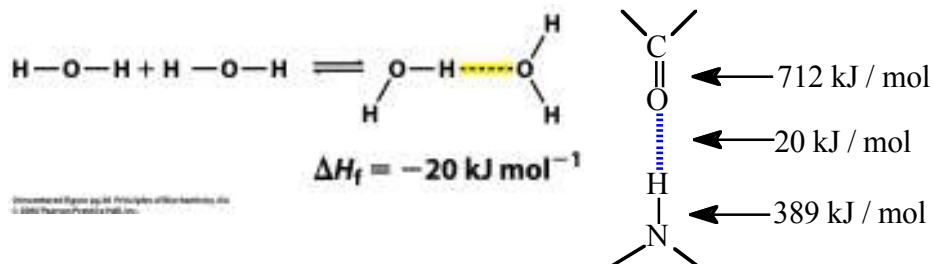


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H-bond: An **electrostatic** attraction between polarized molecules containing O-H, N-H, or F-H.

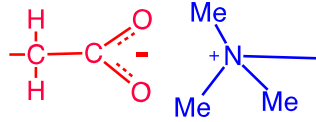
H-bonds are strongest when linear *i.e.* the two heavy atoms and the shared H are in a line.

H-bonding is a **Weak Interaction** compared to covalent bonding - 8-21 kJ / mol.

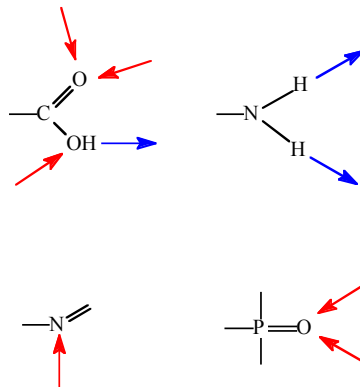


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Electrostatic Interactions: Attraction between oppositely charged ions or repulsion between similarly charged ions - up to 200 kJ / mol.



Some important H-bond **donors** and **acceptors** in cells:



Breaking H-bonds requires the addition of **enthalpy**.

For ice $\Delta H_{\text{Melting}} = +6 \text{ kJ/mol}$

So why does water melt so easily at 25°C?

Because the liquid is more disordered than the solid and $T\Delta S_{\text{melt}} > \Delta H_{\text{melt}}$.

In fact, at 25°C: $T\Delta S_{\text{melt}} = 6.6 \text{ kJ/mol}$

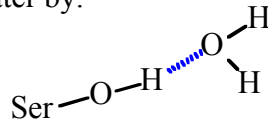
$\Delta H_{\text{melt}} = 6.0 \text{ kJ/mol}$ and

$\Delta G_{\text{melt}} = \Delta H_{\text{melt}} - T\Delta S_{\text{melt}} = -0.6 \text{ kJ/mol}$

So melting is an **entropy-driven** processes.

Biomolecules interact with water by:

1. H-bonding.



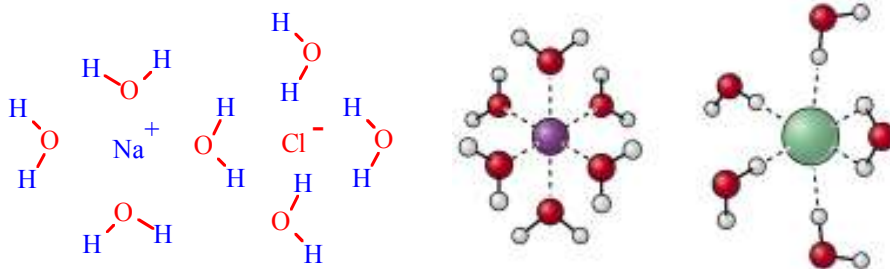
2. Electrostatic interactions:

i. When NaCl dissolves in H₂O, enthalpy is required to break Na⁺ Cl⁻ ionic bonds. +ΔH



ii. Enthalpy is also required to disrupt H-bonding of H₂O. +ΔH

iii. Enthalpy is released when new water-ion interactions form. This is called –“**solvation**”. –ΔH



iv. The net enthalpy change is small and slightly positive.

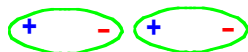
v. Solid NaCl is highly ordered. NaCl in solution is highly disordered. So the large **entropy** increase favours dissolution.

$$\Delta G = \Delta H - T\Delta S$$

$$T\Delta S \gg \Delta H \text{ and } \Delta G < 0$$

3. **van der Waals Interactions:** A short range very weak attraction $\sim 4 \text{ kJ / mol}$.

Non-polar He atoms form a liquid at 4K due to an induced dipole attraction.



Temporary Dipoles

Non-polar hydrocarbons interact with each other by van der Waals interactions.

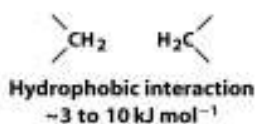
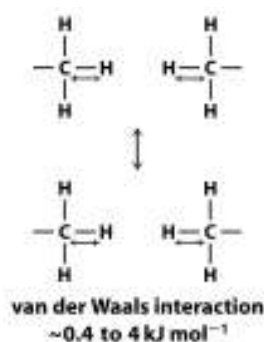
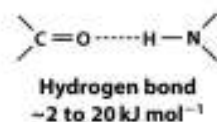
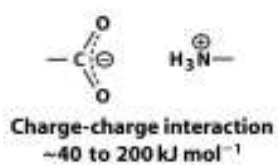
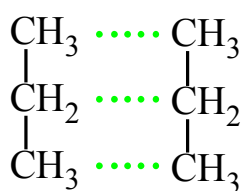


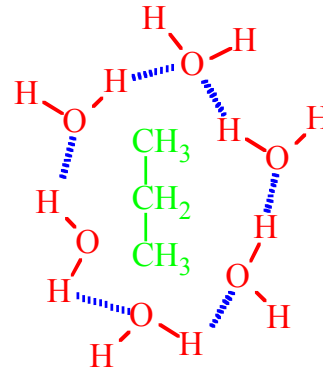
Figure 2-13 Principles of Biochemistry, 4th
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What happens when a non-polar hydrocarbon dissolves in water?

1. Hydrocarbon vdW interactions are broken. $+\Delta H$

2. Water H-bonds are broken. $+\Delta H$

3. New water H-bonds are formed in an organized “cage” around the hydrocarbon. This optimizes the vdW interactions between the hydrocarbon and water, and optimizes the H-bonding among the water molecules. $-\Delta H$



The entropy of water is reduced, disfavoring dissolution of hydrocarbons in water. $-\Delta S$

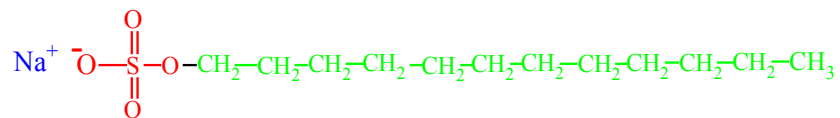
This is called the “[Hydrophobic Effect](#)”.

[Amphipathic](#) molecules contain both polar and non-polar groups. *E.g.* detergents, lipids, proteins, nucleic acids.

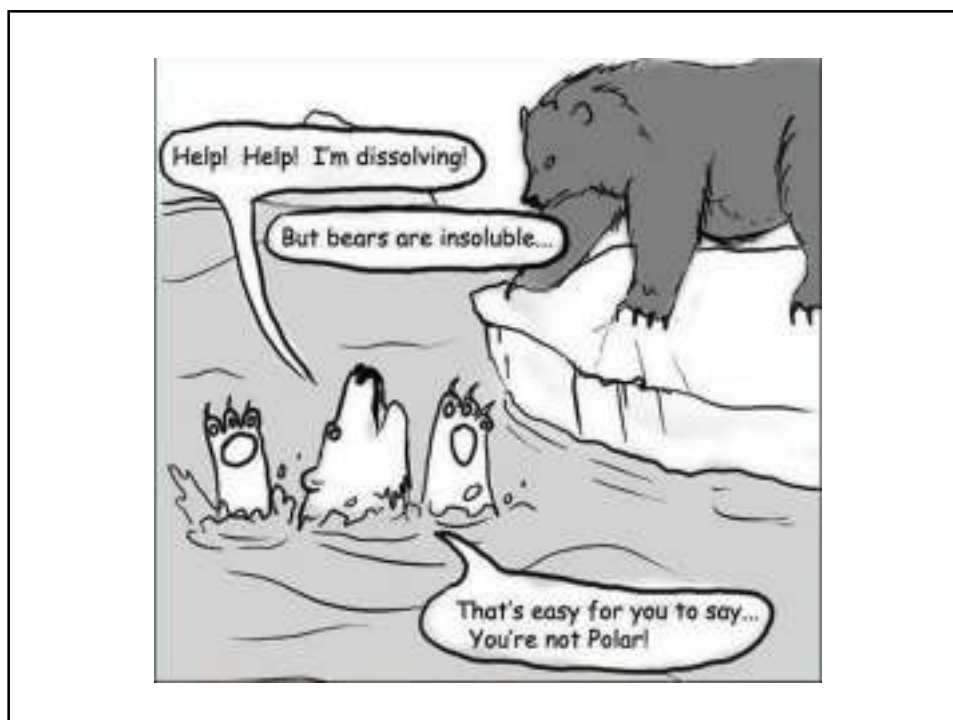
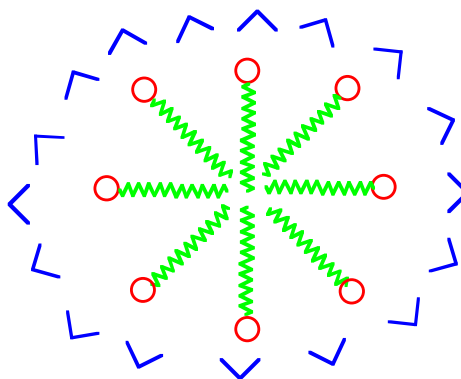
Their lowest free energy states have hydrophobic groups clustered together away from the water, raising the water S.

They help organize detergent micelles, membranes, proteins, and DNA.

A detergent: Sodium dodecylsulphate:



It forms a **micelle** in which the **hydrocarbons** interact with each other *via* vdW to form a hydrophobic core and the **hydrophilic** groups associate with **water**.



Other interactions can occur with the ionized forms of water.



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.8 \times 10^{-16} \text{ M @ } 25^\circ\text{C}$$

$$[\text{H}_2\text{O}] = 55.5 \text{ M (moles / L)}$$

$$\text{So } (K_{\text{eq}} \times 55.5) = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}^2 = K_w$$

Knowing two, you can solve for the third.

$$\text{A convenient way to express } [\text{H}^+] \text{ is pH. } \quad \text{pH} = -\log_{10}[\text{H}^+]$$

In pure water: $[\text{H}^+] = 10^{-7}$ Molar

$$\text{So } -\log_{10}[10^{-7}] = -(-7) = 7 = \text{pH}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

In pure water – $[\text{OH}^-] = 10^{-7}$ Molar

$$-\log_{10}[10^{-7}] = -(-7) = 7 = \text{pOH}$$

When $\text{pH} = \text{pOH}$ we say
water is “**neutral**”

TABLE 2.3 Relation of $[\text{H}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ to pH

pH	$[\text{H}^{\oplus}]$ (M)	$[\text{OH}^{\ominus}]$ (M)
0	1	10^{-14}
1	10^{-1}	10^{-13}
2	10^{-2}	10^{-12}
3	10^{-3}	10^{-11}
4	10^{-4}	10^{-10}
5	10^{-5}	10^{-9}
6	10^{-6}	10^{-8}
7	10^{-7}	10^{-7}
8	10^{-8}	10^{-6}
9	10^{-9}	10^{-5}
10	10^{-10}	10^{-4}
11	10^{-11}	10^{-3}
12	10^{-12}	10^{-2}
13	10^{-13}	10^{-1}

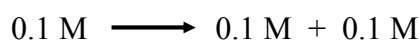
Table 2.3: Principles of Biochemistry, 4/e
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pH can range from 0 to 14.

Below pH 7 water is **“acidic”** –
gastric juice is pH 1.

Above pH 7 it is **“basic”** -
egg white is pH 8.

Strong Acids HCl is a strong acid.



The **acid dissociates completely** and
the pH ~ 1.

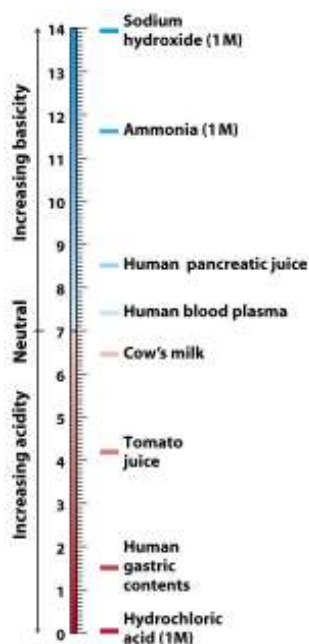
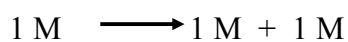


Figure 2-15 Principles of Biochemistry, 4/e
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Strong Bases NaOH is a strong base.



Complete dissociation gives pOH ~ 0 pH ~ 14.

Remember $10^0 = 1$

Most biological acids and bases are **weak**. *i.e.* they undergo **incomplete dissociation**.



Weak Acid

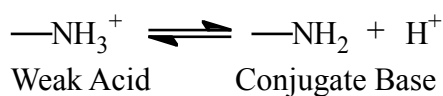
Conjugate Base

A weak acid is a **donor** of protons.



A weak base is an **acceptor** of protons.

Biochemists choose to express all weak acids and bases as “*weak acids*”, so:



In general,



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad \text{HA} \rightleftharpoons \text{A}^- + \text{H}^+$$

K_a is the acid dissociation constant. $\text{p}K_a = -\log_{10}[K_a]$

The weakest acids have the largest $\text{p}K_a$'s.

TABLE 2.4 Dissociation constants and $\text{p}K_a$ values of weak acids in aqueous solutions at 25°C.

Acid	$K_a(\text{M})$	$\text{p}K_a$
HCOOH (Formic acid)	1.77×10^{-4}	3.8
CH ₃ COOH (Acetic acid)	1.76×10^{-5}	4.8
CH ₃ CHOHCOOH (Lactic acid)	1.37×10^{-4}	3.9
H ₃ PO ₄ (Phosphoric acid)	7.52×10^{-3}	2.2
H ₂ PO ₄ [−] (Dihydrogen phosphate ion)	6.21×10^{-8}	7.2
HPO ₄ ^{2−} (Monohydrogen phosphate ion)	2.20×10^{-13}	12.7
H ₂ CO ₃ (Carbonic acid)	4.30×10^{-7}	6.4
HCO ₃ [−] (Bicarbonate ion)	5.61×10^{-11}	10.2
NH ₄ ⁺ (Ammonium ion)	5.62×10^{-10}	9.2
CH ₃ NH ₃ ⁺ (Methylammonium ion)	2.70×10^{-11}	10.7

The $\text{p}K_a$ of acetic acid is 4.76, the $\text{p}K_a$ of ammonia is 9.25.

Table 2.4 Principles of Biochemistry, 4th
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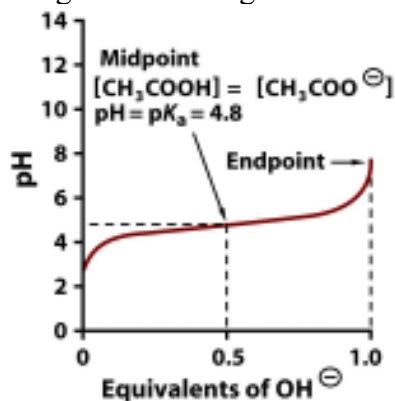
Often, biochemical reactions release H^+ or OH^- . How do cells deal with this? With **Buffers**.

Titration Curves indicate the pH values of different mixtures of a weak acid and its conjugate base. The mixtures are produced by adding different amounts of a strong acid or strong base to the mixture.

The pH of a 0.1 M solution of CH_3COOH is about 1.8.

Addition of 10 mL of 0.1 M NaOH to 100 mL of 0.1 M CH_3COOH raises the pH to 3.7.

What happened?



10 mL of 0.1 M NaOH contains 0.001 moles = 1 millimole of OH^- .

$$\frac{0.1 \text{ moles}}{1000 \text{ ml}} = \frac{x}{10 \text{ ml}} \quad x = 10 \text{ ml} \cdot \frac{0.1 \text{ moles}}{1000 \text{ ml}} = 0.001 \text{ moles}$$

100 mL of 0.1 M CH_3COOH contains 10 millimoles of acid.

So we added 1 millimole or 0.1 equivalent of OH^- = 10% of the acid present.

Some of the added OH^- reacted with H^+ to yield H_2O .

The **Law of Mass Action** (AKA LeChatelier's Principle) then caused the HA to ionize to release more protons. This continued until all the added OH^- was neutralized.

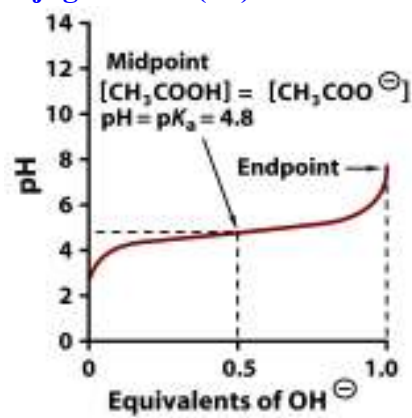


So $[HA]$ has decreased, $[A^-]$ increased, $[H^+]$ decreased, $[OH^-]$ increased, and pH increased.

The added OH^- (a strong base) will neutralize an equal # of moles of HA (a weak acid). Similarly, a strong acid will neutralize an equal # of moles of conjugate base (A^-).

When 50 mL of NaOH have been added, 5 millimoles of OH^- have been added, neutralizing half of the HA.

The acid is half neutralized and so half dissociated $[HA] = [A^-]$
i.e. $[Weak\ Acid] = [Conjugate\ Base]$



Remember,
$$K_a = \frac{[H^+][A^-]}{[HA]} \quad [H^+] = \frac{K_a[HA]}{[A^-]}$$

So when $[HA] = [A^-]$, $[H^+] = K_a$ and $pH = pK_a$

Near the end of the curve, when there is no more HA to ionize, the pH will rise sharply.

The same graph could have been produced by adding HCl (a strong acid) to a solution of sodium acetate, the conjugate base of acetic acid (a weak base).

Features of titration curves.

1. At the ends of the curves small additions of acid and base result in large changes in pH.

2. In the middle, small additions of strong acid or base cause small changes in pH. The region where $\text{pH} = \text{pK}_a$ is called the buffering region.

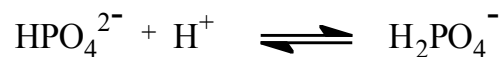
A Buffer is a mixture of WA and CB that resists changes in pH when small additions of strong acid or base are added.

How does it work? Near the pK_a $[\text{WA}] \sim [\text{CB}]$.

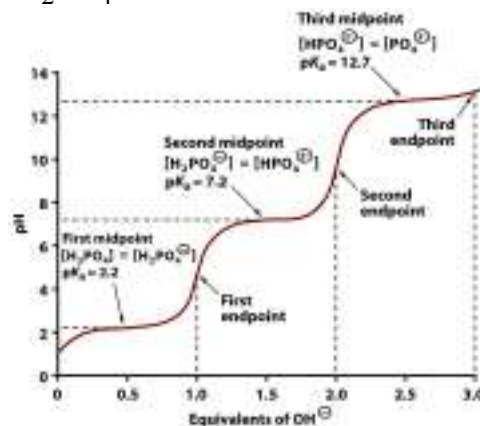
The WA can neutralize added OH^- , and the CB can neutralize added H^+ .

Cells require buffers because high concentrations of H^+ and OH^- can break covalent bonds.

The main buffer system found in cells is :



The pK_a of H_2PO_4^- is 7.2.



We can re-write $[H^+] = \frac{K_a[HA]}{[A^-]}$ in terms of pH and pK_a

$$pH = pK_a - \log_{10} \left\{ \frac{[HA]}{[A^-]} \right\}$$

Or

$$pH = pK_a + \log_{10} \left\{ \frac{[A^-]}{[HA]} \right\}$$

Using this [Henderson-Hasselbach Equation](#) we can calculate the pH of a WA-CB pair if we know their ratio and the pK_a .

WA-CB pairs buffer well as long as: $\frac{1}{10} < \frac{[CB]}{[WA]} < \frac{10}{1}$

$$pH = pK_a + \log_{10} \left\{ \frac{[1]}{[10]} \right\} = pK_a - 1.0$$

$$pH = pK_a + \log_{10} \left\{ \frac{[10]}{[1]} \right\} = pK_a + 1.0$$

For acetic acid the range is: 3.76 to 5.76.

Example Calculation: What is the pH of a 20 mL solution of 0.1 M Tris base (RNH_2) after addition of 10 mL of 0.1 M HCl? The $pK_a = 8.1$

First we calculate that we have 2 mmoles of Tris base and 1 mmole of HCl.

The reaction will be:



The above means that 1 mmole of strong acid has neutralized 1 mmole of conjugate base giving 1 mmole of WA and 1 mmole of CB.

From HH: $pH = 8.1 + \text{Log}\left\{\frac{1\text{mmol} / 30\text{ml}}{1\text{mmol} / 30\text{ml}}\right\}$

So $pH = 8.1 + 0 = 8.1$