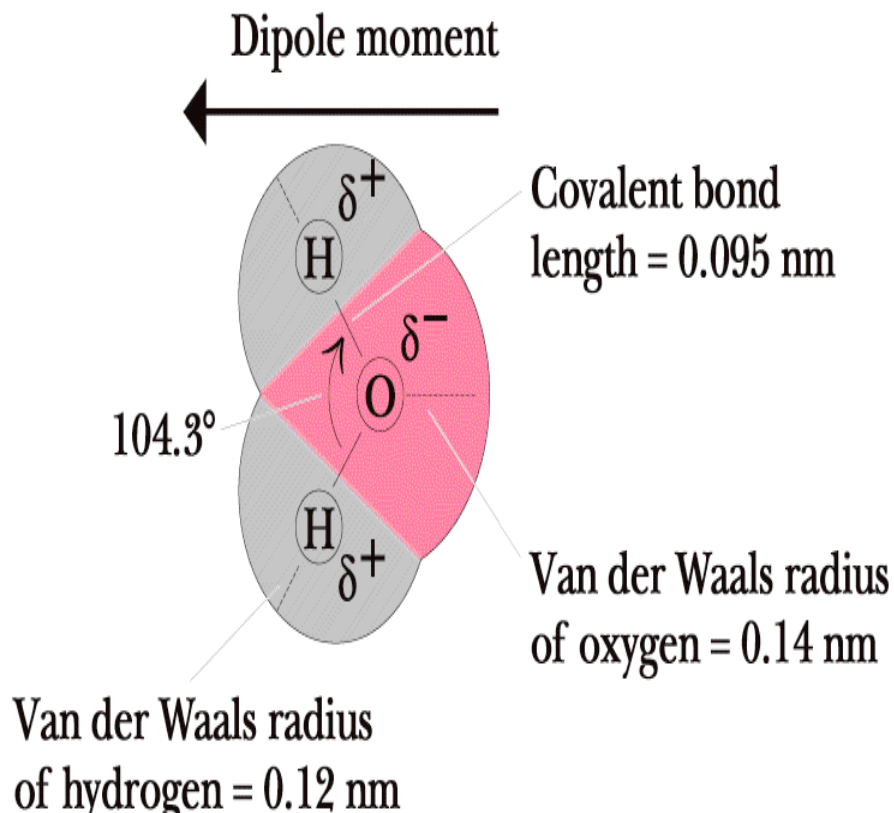


Water, pH, Ionic Equilibria, and the Hydrophobic Effect

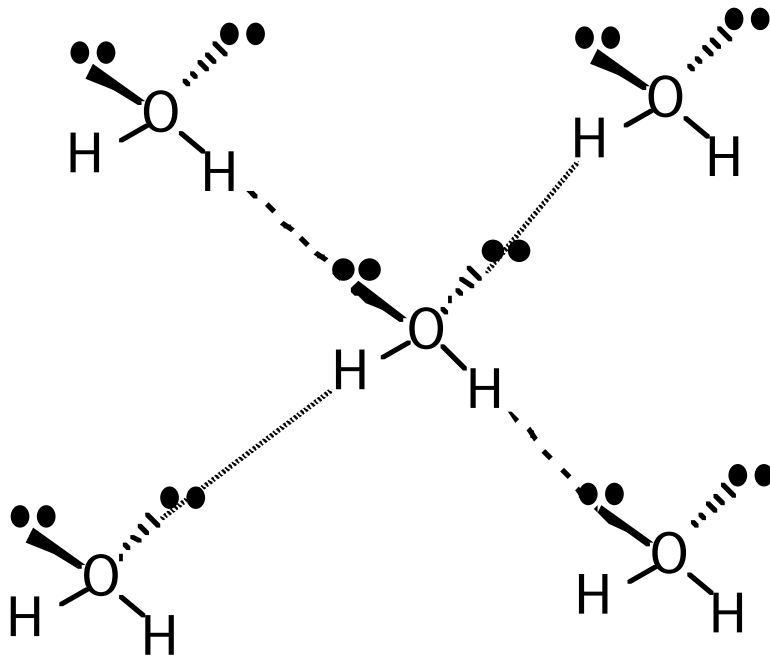
- Water is the medium of life.
- Organisms are typically constituted of 70-90% water.
- Water and its ionization products, hydrogen ions (protons) and hydroxide ions, are critical determinants of the structure and function of proteins, nucleic acids, and membranes.

Structure of Water



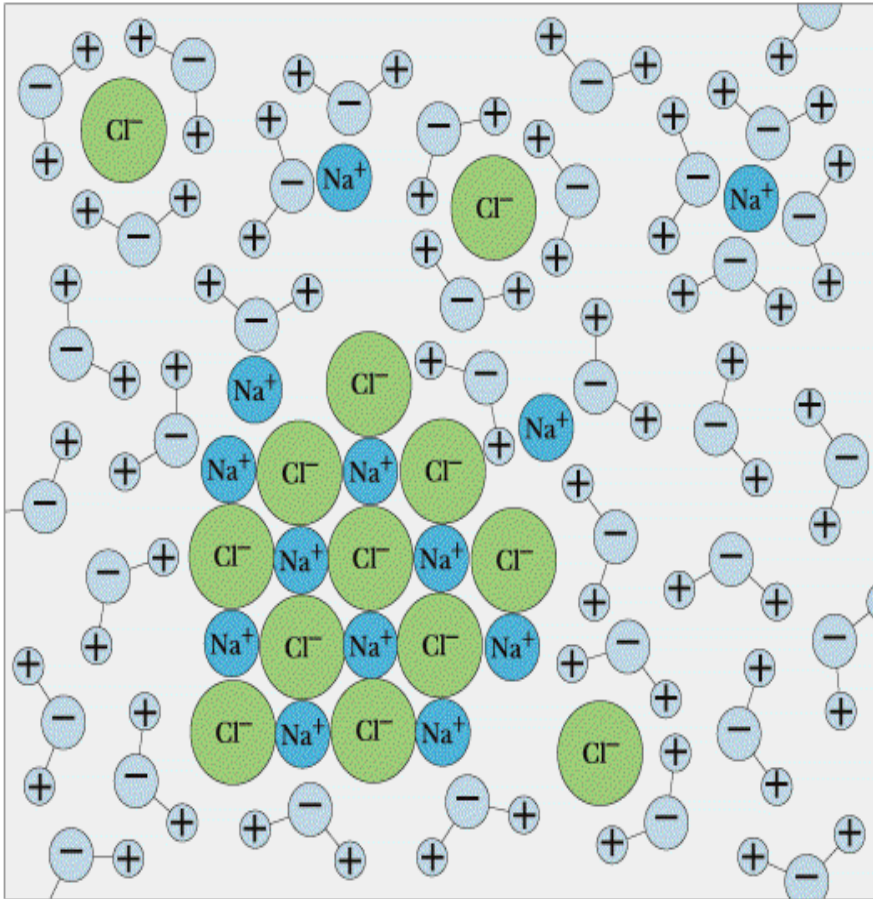
- Water has two hydrogen atoms covalently linked to a central oxygen atom.
- Two lone pairs of electrons occupy other two sp^3 orbitals.
- **Structure is a distorted tetrahedron.**
- This geometry, and the electronegativity of the oxygen atom induces a net dipole moment.
- Normal tetrahedral bond angle (as in methane) is 109.5°
- **Because of the dipole moment, water can serve as both a hydrogen bond donor and acceptor.**
- **What structure would you expect for CO₂? Would it have a dipole moment? Is it polar? Can it hydrogen bond?**

Hydrogen Bonding in Water



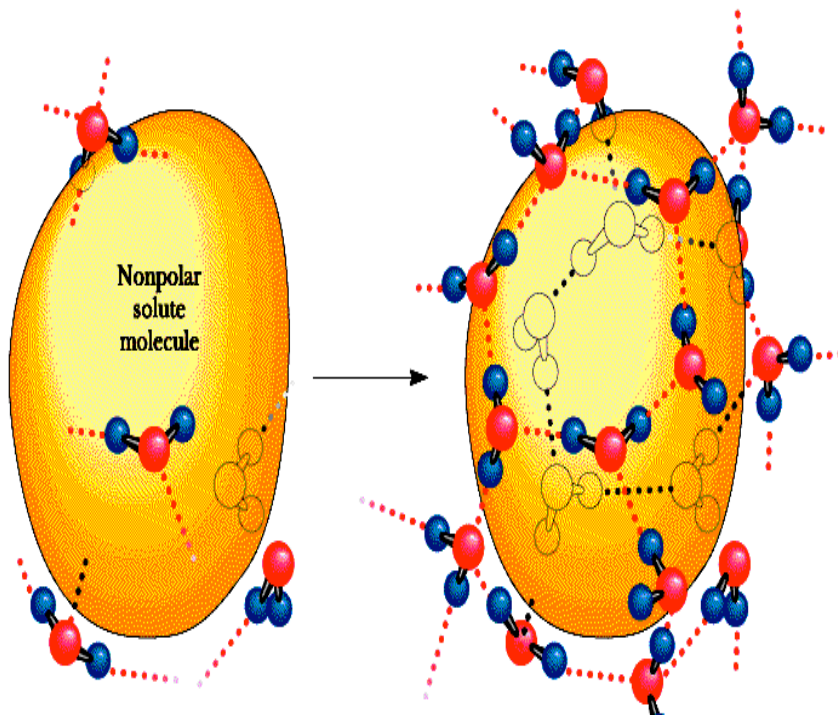
- Water can serve as both an **H donor** and an **H acceptor** in H-bond formation
- It is the potential to form four H-bonds per water molecule that endows it with an anomalously high boiling point, melting point, heat of vaporization, and surface tension. *Can you reason why?*
- Hydrogen bonding in water is cooperative. A water molecule that acts as a hydrogen bond donor is a better hydrogen bond acceptor.
- Hydrogen bonds between neighboring molecules are weak (23 kJ/mole) relative to the H-O covalent bonds (420 kJ/mol)

Solvent Properties of Water



- Because water is highly polar, it is an ideal solvent for ionic substances, or polar substances such as sugars, small alcohols, amines, and carbonyl-containing molecules such as aldehydes and ketones.
- Water dissolves salts because of strong electrostatic interactions.
- The attraction between water molecules interacting with ions is much greater than that of the ion with its oppositely charged partner.
- The diminished attraction is a measure of water's **dielectric constant**.

Hydrophobic Interactions



- Nonpolar substances do not readily hydrogen bond to water, and have a highly reduced solubility.

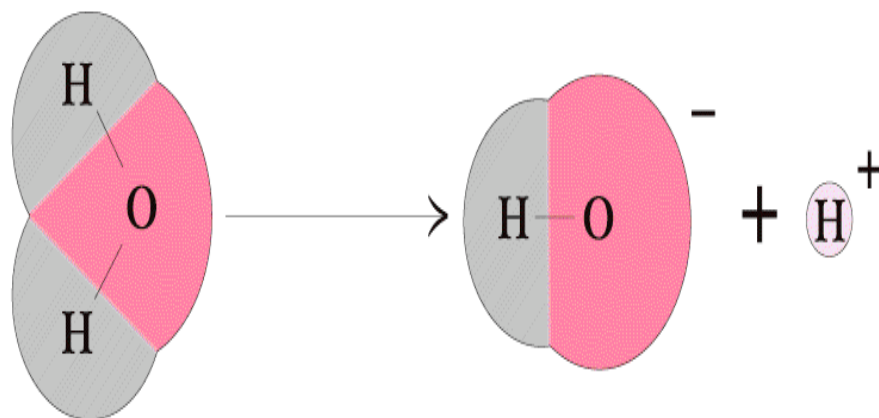
Water forms a **clathrate** or **hydration shell** around nonpolar substances.

In this hydration shell, the water molecules are very ordered, which makes this an **entropically unfavorable condition**.

It is less costly to have one big hydration shell rather than many smaller ones, because a joint hydration shell will have less surface area.

Therefore, **hydrophobic molecules experience a net attraction which is entropically driven**. This is called the **hydrophobic effect**.

The Ionization of Water

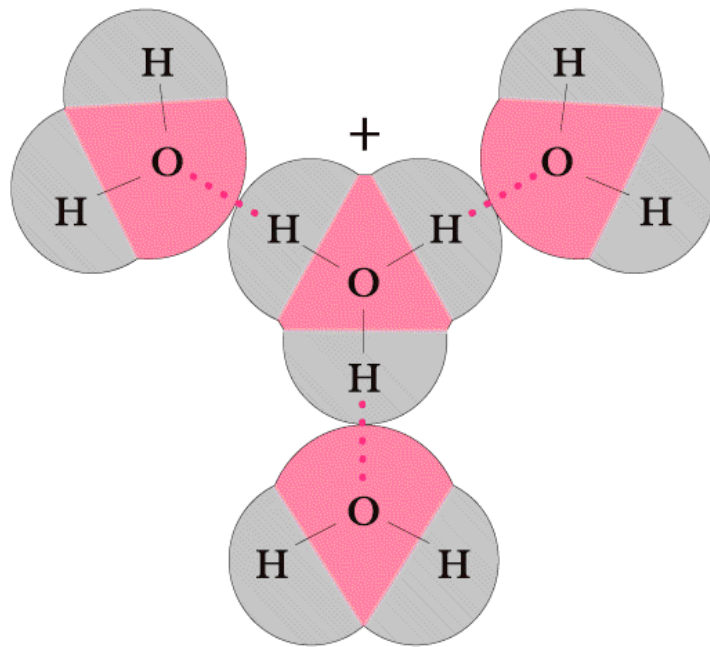


- Because of the high electronegativity of oxygen, the electrons in the O-H bond of water tend to be significantly more closely associated with oxygen rather than hydrogen. This permits the hydrogen to dissociate, leaving its electron with oxygen. The formal charge on oxygen becomes -1, while that of hydrogen becomes +1.

Remember, on both sides of the arrow, the total formal charge must remain the same.

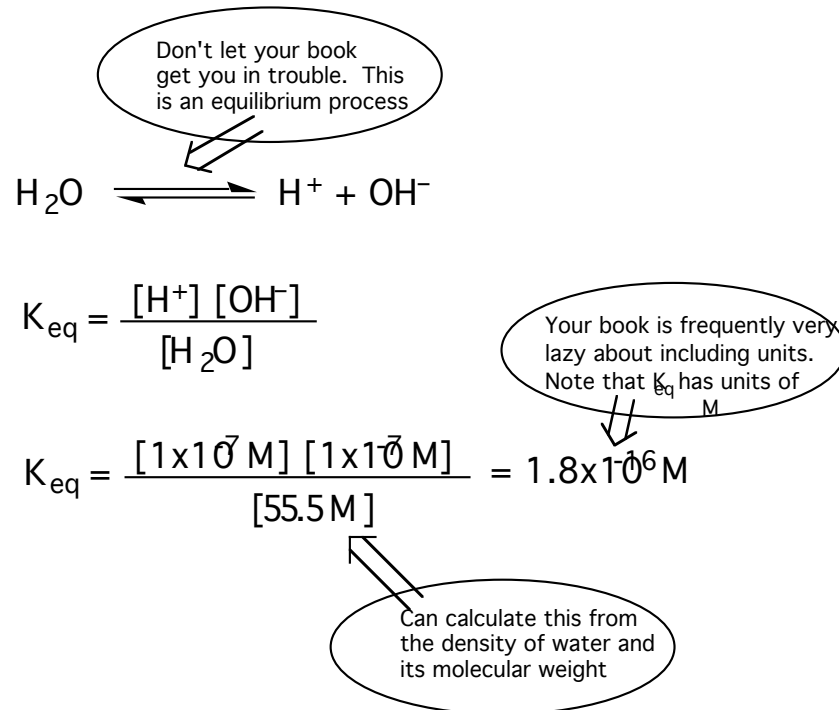
A hydrogen without electrons is called a **hydrogen ion** or a **proton**. A hydrogen with 1 electron is called a **hydrogen atom**. A hydrogen with 2 electrons is called a **hydride**. The other resulting species (OH⁻) is called a **hydroxide ion**.

Proton Hydration



- Protons do not exist free in solution. They are immediately hydrated to form **hydronium ions**. A **hydronium ion** is a water molecule with a proton associated with one of the non-bonding electron pairs. This bond is covalent, although the proton readily dissociates. **Note the formal charge on the hydronium ion**, as well as the hydrogen bonding pattern. **The covalent and hydrogen bonds are interchangeable**. This allows for an extremely fast mobility of protons in water via "proton jumping."

The Dissociation of Water



Define a new constant K_w , which is equal to the concentration of water multiplied by K_{eq} . K_w is called the ion product of water.

$$K_{\text{eq}} \times 55.5 \text{ M} = 1.8 \times 10^{-16} \times 55.5 \text{ M} = 1 \times 10^{-14} \text{ M}^2 = K_w$$

- An equilibrium equation can be written for the dissociation of water. At 25°C, water dissociates to the extent that $[\text{H}^+]$ and $[\text{OH}^-]$ are $1 \times 10^{-7} \text{ M}$. **The concentration of water is for all practical purposes a constant, and is 55.5 M.**
- The ion product of water, K_w , is the product of the equilibrium constant and the concentration of water, and is $1 \times 10^{-14} \text{ M}^2$.
- **In water, the product of the concentrations of $[\text{H}^+]$ and $[\text{OH}^-]$ must always be $1 \times 10^{-14} \text{ M}^2$.**
- **Sorry about the print-out of some of the numbers on the left!**

What is pH?

$$1 \times 10^{-14} \text{M}^2 = K_w = [\text{H}^+] [\text{OH}^-]$$

$$-\log(1 \times 10^{-14}) = -\log K_w = \log [\text{H}^+] [\text{OH}^-]$$

$$14 = \text{p}K_w = \text{pH} + \text{pOH}$$

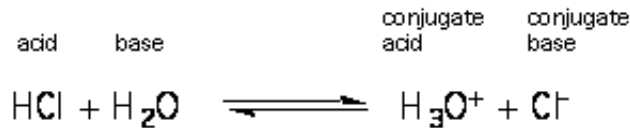
$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

- To avoid the cumbersome use of large negative exponents, the pH scale was devised. **pH is defined as the negative logarithm of the hydrogen ion concentration.**

We can simplify our equation relating the ion product of water to proton and hydroxide ion concentrations by taking the negative logarithm of both sides of the equation.

- Notice that when the hydroxide ion and hydrogen ion concentrations are the same, the pH is 7, and is termed neutral.
- It is also possible for the pH to be negative; however, the pH and pOH must always add to 14.

Dissociation of Strong Electrolytes



$$K = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{H}_2\text{O}][\text{HCl}]}$$

$$K_a = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]}$$

Some strong acids and their dissociation constants

1. HClO₄ (Perchloric acid) $K_a \ll 1 \times 10^0$
2. HI (Iodic acid) $K_a = 1 \times 10^0$
3. H₂SO₄ (Sulfuric acid) $K_a \ll 1 \times 10^0$
4. HBr (Bromic acid) $K_a = 1 \times 10^0$
5. HCl (Hydrochloric acid) $K_a \ll 1 \times 10^0$

The K_a for H₃O⁺ = 55

What is the pH of a 0.1 M solution of NaOH?

NaOH is a strong base

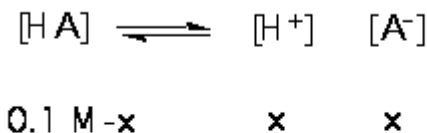
- Strong **electrolytes** are substances that are almost completely dissociated in solution. These include strong acids and bases as well as main salts (e.g. NaCl and K₂SO₄).
- The dissociation of strong acids can be treated as a proton transfer event with a corresponding equilibrium equation. The product of the equilibrium constant and the concentration of water (55.5) defines the acid dissociation constant, K_a .
- For strong acids, K_a is exceedingly large, and by comparison, the concentration of undissociated acid is vanishingly small.
- Therefore, for strong acids, the pH of an aqueous solution simply reflects the final concentration of added acid.
- For strong bases such as NaOH, the pOH is simply the final concentration of added base.
- What's the pH of a 1 mM solution of HCl?

Dissociation of Weak Electrolytes



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.74 \times 10^{-5} \text{M}$$

What is the final pH of a solution when 0.1 mol of acetic acid is adjusted to 1 L of water?



$$K_a = \frac{[x][x]}{[0.1 \text{ M} - x]} = 1.74 \times 10^{-5} \text{M}$$

$$x^2 = 1.74 \times 10^{-5} - 1.74 \times 10^{-5}x$$

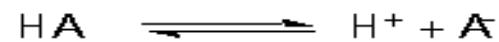
$$x^2 + 1.74 \times 10^{-5}x - 1.74 \times 10^{-5} = 0$$

solve quadratic equation

Equation can be simplified by noting that 0.1 M - x is really just 0.1 M, because x is small compared to 0.1.

- Weak electrolytes are substances having only a slight tendency to form ions in solution. This makes determining the pH of solutions of weak acids a little more difficult than in the case of strong acids.
- The equation will be in the form of a quadratic, which must be solved.
- The equation frequently can be simplified by noting that the amount of dissociated species is much less than the amount of undissociated acid.

Henderson-Hasselbalch Equation



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \qquad [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

$$\log[\text{H}^+] = \log K_a + \log[\text{HA}] - \log[\text{A}^-]$$

$$-\log[\text{H}^+] = -\log K_a - \log[\text{HA}] + \log[\text{A}^-]$$

$$\text{pH} = \text{p}K_a + \log \frac{\text{A}^-}{\text{HA}}$$

Note that when the concentrations of the conjugate acid and conjugate base are equal, the $\text{pH} = \text{p}K_a$.

What is the pH when 100 mL of 0.1 N NaOH is added to 150 mL of 0.2 M Acetic acid? The $\text{p}K_a$ of acetic acid is 4

Sodium hydroxide is a strong base. It will neutralize all of the acid present stoichiometrically. 100 mL of 0.1 N NaOH = 0.01 mol of hydroxide ion. Assume that the acid is essentially undissociated. Therefore 150 mL of 0.2 M acetic acid = 0.03 mol. Since we are looking at ratios of acid and conjugate base, there is no need to calculate concentrations.

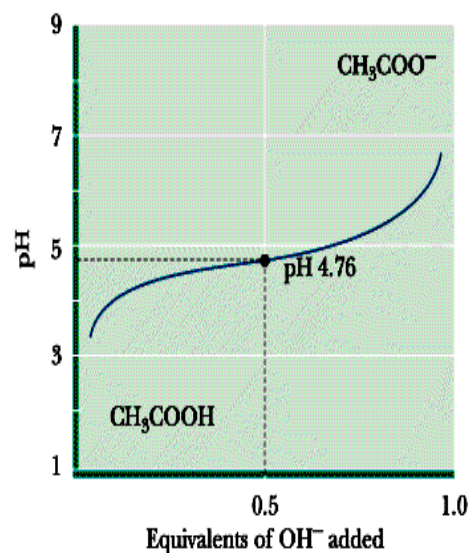
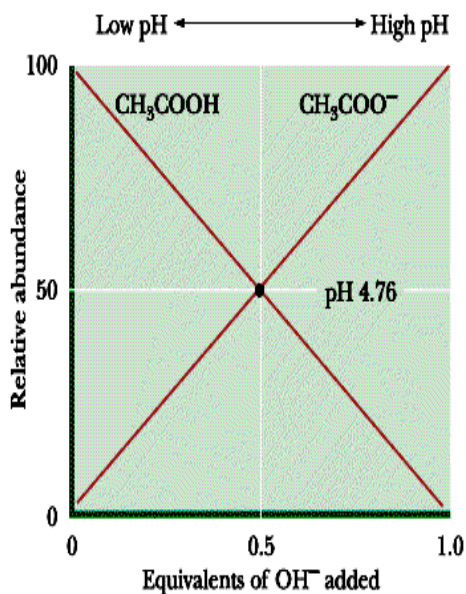
$$\text{pH} = 4.76 + \log \frac{0.01}{0.02} = 4.46$$

Dissociation Constants of Some Weak Acids

Acid	K_a (M)	pK_a
Formic acid	1.78×10^{-4}	3.75
Acetic acid	1.74×10^{-5}	4.76
Ammonium ion	5.62×10^{-10}	9.25
Imidazole	1.02×10^{-7}	6.99
Histidine (side chain)	9.12×10^{-7}	6.04
Glycine (carboxylate)	4.47×10^{-3}	2.35
Glycine (amino)	1.66×10^{-10}	9.78
Carbonic acid 1	1.70×10^{-4}	6.37
Carbonic acid 2	5.75×10^{-11}	10.20
Phosphoric acid 1	7.08×10^{-3}	2.14
Phosphoric acid 2	6.31×10^{-8}	7.20
Phosphoric acid 3	3.98×10^{-13}	12.40

It's not necessary to memorize this slide; however, you should be adept at using the numbers appropriately.

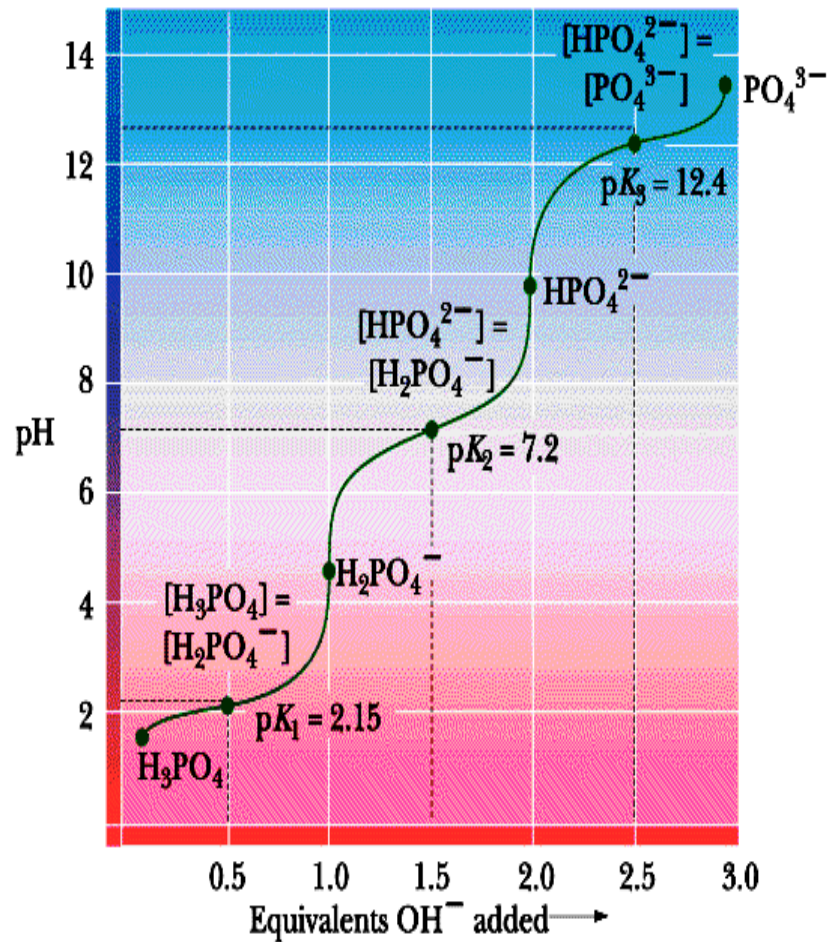
Titration Curves



Notice the difference in the two curves, which describe the exact same experiment. The curve at right describes the pH as a function of added base. **This is a logarithmic function.**

- To **titrate** is to slowly add known amounts of one species to another (such as acid to base) in order to determine the quantity or concentration of the initial species.
- The titration of acetic acid with NaOH is shown. NaOH is a strong base; therefore, any amount added will stoichiometrically neutralize an equivalent amount of acid.
- Because acetic acid is a weak acid, most of it will exist in the protonated form at the beginning of the titration.
- Experimentally, acid-base titrations are carried out while simultaneously monitoring the pH of the solution. When concentrations of acid and base are equal, the pK_a of the species has been reached. This results in an inflection point in the titration curve.

Polyprotic Acids

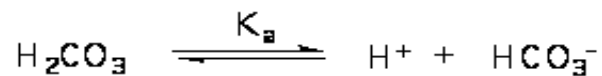
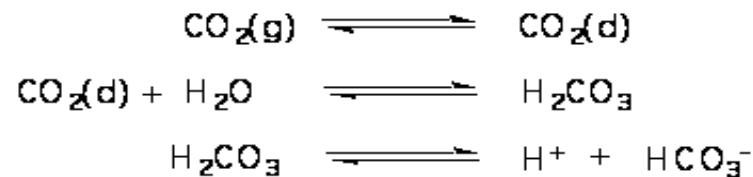


- The adjacent figure shows the titration curve of phosphoric acid. Note that in the fully protonated form, it contains 3 protons (hydrogen ions). Note the formal charges for each deprotonated state.
- Note that each deprotonation has a distinct pKa associated with it. Note the slopes of the curve around the pKa values, and the slopes between two pKa values.
- As stated earlier, the inflection points along the shallower slopes are the pKas, and the inflection points along the steeper slopes are called the equivalence points.
- Around the pKas of titration curves, the addition of acid or base doesn't change the pH much. Outside of this region it changes drastically. Around the pKa, the weak acid and conjugate base system behave as a buffer.
- Buffers function to resist changes in pH as small amounts of acid or base are added.

Sample Problem

- **Try this problem at home!**
- What are the approximate fractional concentrations of the following phosphate species at pH values of 0, 2, 4, 6, 8, 10, and 12?
- H_3PO_4
- H_2PO_4^-
- HPO_4^{2-}
- PO_4^{3-}
- The three relevant pKa values are 2.15, 7.2, and 12.4

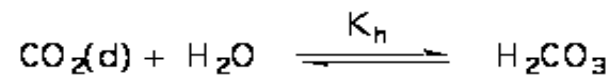
The Bicarbonate Buffering System



$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{K_h[\text{CO}_2(\text{d})]}$$

$$K_a K_h = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(\text{d})]}$$



equilibrium lies far to the left.
facilitated by the enzyme carbonic anhydrase

$$K_h = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(\text{d})]}$$

$$\text{Let } K_a K_h = K_{\text{overall}}$$

The value of $K_a = 0.000269$

The value of $K_h = 0.003$

$$K_{\text{overall}} = 8.07 \times 10^{-7}$$

$$\text{p}K_{\text{overall}} = 6.1$$

Problem is that the $\text{p}K_a$ of blood, where this system is important is about 7.4. Therefore, it appears that this would not be a good buffer since there is not enough of the acid component to neutralize the base. Because of the enzyme carbonic anhydrase, the acid component is effectively equal to the amount of $\text{H}_2\text{O} + \text{CO}_2$.