

- **Autoionization of Water**



$$K = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] = 1.802 \times 10^{-16}$$

Concentration of  $[\text{H}_2\text{O}]$  is so HIGH autoionization is just a drop in the bucket, so  $[\text{H}_2\text{O}]$  stays  $\approx$  constant at 55.5 M, So, we'll define a new constant,  $K_w$

$$K_w = K \times [\text{H}_2\text{O}] = 1.802 \times 10^{-16} \times 55.5$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.000 \times 10^{-14}$$

Take  $[-\log]$  of **left** and **right** hand sides of equation:

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

Left hand side

$$(-\log \text{H}^+) + (-\log \text{OH}^-) = \text{pH} + \text{pOH}$$

Right hand side

$$= (-\log 1) + (-\log 10^{-14}) = 14$$

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

This is always true, you can always get the concentration of  $\text{H}^+$  or  $\text{OH}^-$  by knowing just one, and using the equation above.

$$\text{pH} = 1$$

$$\text{pOH} \underline{\hspace{1cm}}$$

$$\text{OH}^- \underline{\hspace{1cm}}$$

$$\text{pH} = 5$$

$$\text{pOH} \underline{\hspace{1cm}}$$

$$\text{OH}^- \underline{\hspace{1cm}}$$

$$\text{pH} = 7$$

$$\text{pOH} \underline{\hspace{1cm}}$$

$$\text{OH}^- \underline{\hspace{1cm}}$$

So, at  $\text{pH} = 7$ ,  $\text{H}^+ = \text{OH}^- = 10^{-7}$  solution is **neutral**

- **Bases:** The Brønsted base is defined as any substance that can accept a hydrogen ion. In essence, a base is the opposite of an acid. Bases feel slippery and soapy to the touch. Bases will be able to remove a  $\text{H}^+$  from water, and thus make a solution have more hydroxide ions ( $\text{OH}^-$ ) than you have normally in neutral pure water where  $\text{H}^+ = \text{OH}^- = 10^{-7}$  M ( $\text{pH}=7$ ). When  $[\text{OH}^-]$  goes up, the concentration of  $\text{H}^+$  goes down you have an excess of hydroxide ions  $\text{OH}^-$  and therefore a high pH.
  - $\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$  strong base, pH high,  $>10$
  - $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$  weak bases, pH 7-9 region

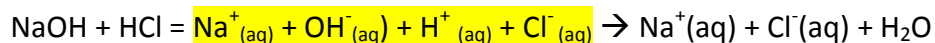
Base and its Conjugate Acid: Which species is the conjugate acid of B?

As the strength of a base increases, the strength of its conjugate acid \_\_\_\_\_

Why? \_\_\_\_\_

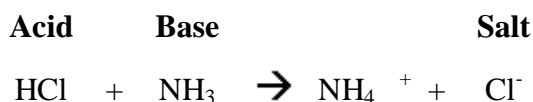
## Acids and Bases and Buffers

**Neutralization Reactions:** As in the neutralization reactions we saw earlier, when NaOH and KOH, react with acids, they form salts and water. Here, you see the base accepted a proton from the acid



Because NaOH and HCl are strong bases and acids, they act like ionic compounds and totally dissociate away from each other in water (just like any ionic salt such as CaCl<sub>2</sub> or NaCl). The yellow highlight above is the formally proper way of writing out the reactants in this neutralization reaction, but it's a lot of work. Most times, we take a shortcut and do not explicitly show all the ion dissociations, and do not include the yellow highlighted step. In this class, it will NOT be necessary to write out the full ionic dissociations unless specifically asked. It is not wrong to do so, but it takes time that you may not have during a quiz or exam.

Not all bases possess an OH<sup>-</sup> ion. Ammonia (NH<sub>3</sub>), for example, acts like a base by accepting a hydrogen ion from an acid as illustrated by the neutralization reaction below:



Reaction between baking soda (NaHCO<sub>3</sub>) and acids (HCl) produces carbonic acid (H<sub>2</sub>CO<sub>3</sub>) which decomposes into CO<sub>2</sub> and water as we saw in lab yesterday for Tums. Let's see what happens if we add HCl to baking soda.....DEMO

- Back to those pKas

$$\text{pKa} = -\log \text{Ka}$$

So, if you know the Ka, the acid dissociation constant, you can calculate a pKa. Earlier this week, we saw that as the pKa increases, the strength of the acid decreases.

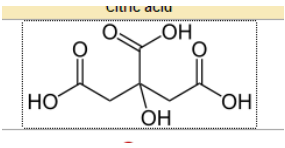
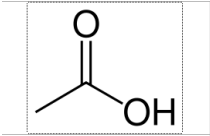
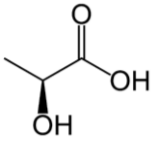
Now hold on for something even better:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$\begin{aligned} \text{Ka} &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \\ -\log \text{Ka} &= -\log \left\{ \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \right\} \\ \text{pKa} &= -\log[\text{H}^+] + \{-\log[\text{A}^-]/[\text{HA}]\} \\ \text{pKa} &= \text{pH} - \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right) \end{aligned}$$

**What happens when  $[\text{A}^-]/[\text{HA}] = 1$**  \_\_\_\_\_

If you have a mixture of a weak acid HA and its conjugate base A<sup>-</sup>, approx equal concentrations, and at a pH close to the pKa, then you have a situation where even if you add a strong acid directly to the solution, the pH won't change much because the HA/A<sup>-</sup> ratio will adjust itself and stay close to 1. This is called a BUFFERED solution.

## pH of Common Solutions of Acids and Bases

	[H <sup>+</sup> ]	pH	Example	Structure
Acids	1 x 10 <sup>0</sup>	0	1 M HCl	H <sup>+</sup> Cl <sup>-</sup>
	1 x 10 <sup>-1</sup>	1	Stomach acid (0.1 M HCl)	H <sup>+</sup> Cl <sup>-</sup>
	1 x 10 <sup>-2</sup>	2	Lemon juice	
	1 x 10 <sup>-3</sup>	3	Vinegar- CH <sub>3</sub> COOH	
	1 x 10 <sup>-4</sup>	4	Soda (mostly due to carbonation)	H <sub>2</sub> CO <sub>3</sub>
	1 x 10 <sup>-5</sup>	5	Rainwater (pH even lower in acid rain)	
	1 x 10 <sup>-6</sup>	6	Milk (lactic acid – C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> )	
Neutral	1 x 10 <sup>-7</sup>	7	Pure water	
Bases	1 x 10 <sup>-8</sup>	8	Egg whites	
	1 x 10 <sup>-9</sup>	9	Baking soda NaHCO <sub>3</sub>	
	1 x 10 <sup>-10</sup>	10	Tums <sup>®</sup> antacid CaCO <sub>3</sub>	
	1 x 10 <sup>-11</sup>	11	Ammonia – NH <sub>3</sub>	
	1 x 10 <sup>-12</sup>	12	Mineral lime - Ca(OH) <sub>2</sub>	
	1 x 10 <sup>-13</sup>	13	Drano <sup>®</sup>	
	1 x 10 <sup>-14</sup>	14	Sodium Hydroxide NaOH	

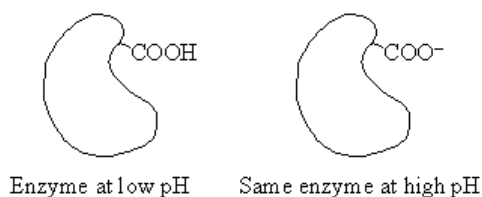
## Acids and Bases and Buffers

Biological Systems: All living things are water-based systems, which means that they depend heavily on aqueous equilibria, especially acid-base equilibria. Therefore, all the acid-base and pH concepts we have discussed so far are extremely important to **biochemistry**, which is the study of the chemistry of biological systems.

Reasons why we should be concerned about pH in biological systems:

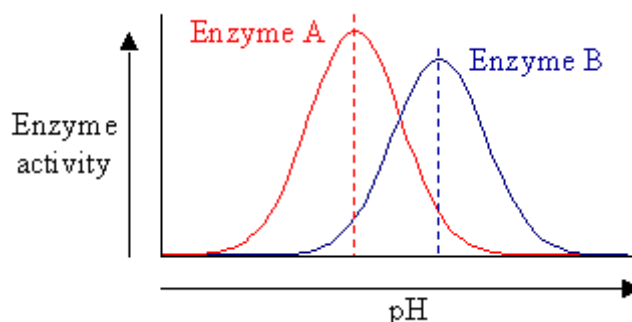
- It gives a qualitative measure for many problems in cell biology and related fields
- Proton dissociable groups are found in macromolecules (such as proteins) as well as the small molecules we have discussed already
- The cell environment is always buffered at approximately pH 7
- Experiments such as biological enzymatic assays require a certain pH

Just as in other acid-base systems, biological macromolecules act as acids and bases by donating and accepting protons. However, due to the size of these molecules, they often contain several different groups that accept or donate protons instead of just one such group. Thus, we talk about macromolecules as *having acidic and basic groups* rather than as *being acids and bases*. These acidic and basic groups act as weak acids and bases, with  $K_a$  values which determine the extent of dissociation of the group depending on the pH of the system. Therefore, changes in the pH around the macromolecule will determine which groups are protonated and which are not, which in turn determines properties of the molecule. This is especially important for **enzymes**, which are proteins that act as catalysts for important biological reactions. Most enzymes only work within a certain pH range.



For example, consider an enzyme with a carboxyl group. The charge of that group will depend on the pH (neutral low pH and negative at high pH). If the enzyme needs to be negatively charged (de-protonated) in order to be active, then the enzyme will only work at higher pH's in which the majority of

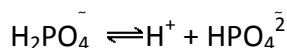
the enzyme molecules have their carboxyl group de-protonated. At very high pH's the protein may denature and this will also make it not be active. In this way, pH determines which enzymes are active and thus which biochemical reactions can occur.



## Buffer Systems in Living Organisms

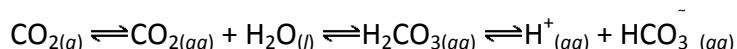
Because all biological processes are dependent on pH, cells and organisms must maintain a specific and constant pH in order to keep their enzymes in the optimum state of protonation.

1. Cytoplasm controlled by the phosphate buffer system:



This system provides the maximum buffering capacity near pH 6.86 (the pKa of  $\text{H}_2\text{PO}_4^-$ ). It provides the buffering effect in intracellular fluid, and is important in urine.

2. Blood must be maintained at pH ~7.4 (pH < 6.9 and >7.6 are life-threatening). The pH of the blood is controlled by the bicarbonate buffer system:



The tissues release  $\text{CO}_2$  into the blood, where it is converted to  $\text{HCO}_3^-$ . In this form, it is carried to the lungs, where it is converted back to gaseous  $\text{CO}_2$  for exhalation. pH depends on  $[\text{H}_2\text{CO}_3]$  and  $[\text{HCO}_3^-]$ , and  $[\text{H}_2\text{CO}_3]$  depends on the  $\text{CO}_2$  dissolved in blood.

### Breathing:

If tissues release  $\text{H}^+$  into blood:

- $[\text{H}^+]$  increases (7.40 to 7.35)
- $[\text{H}_2\text{CO}_3]$  increases
- $[\text{CO}_2]$  dissolved in blood increases
- pressure of  $\text{CO}_2$  in lungs increases
- respiration rates increases, restoring equilibrium
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If tissues release  $\text{OH}^-$  into blood (or remove  $\text{H}^+$  from blood):

- $[\text{H}^+]$  decreases
- $[\text{H}_2\text{CO}_3]$  decreases
- $[\text{CO}_2]$  dissolved in blood decreases
- pressure of  $\text{CO}_2$  in lungs decreases
- respiration rate increases, restoring equilibrium

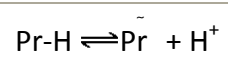
### Major Buffer Systems of the Human Body

Bicarbonate buffer	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	In blood plasma
Hemoglobin	$\text{Hb-H} \rightleftharpoons \text{Hb} + \text{H}^+$	Interior of red blood cells
Phosphate buffer	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	Most important in urine

Acids and Bases and Buffers

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Protein



Intracellular fluid