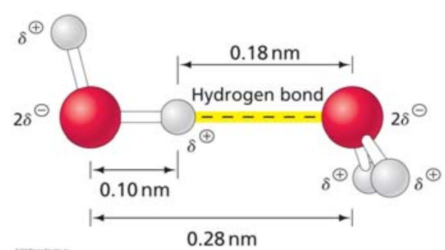
Aqueous Solutions

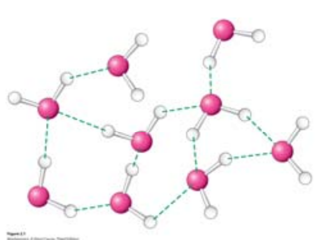
Pratt & Cornely

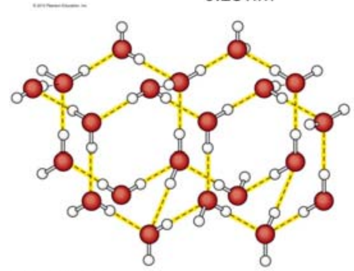
Chapter 2

Water

- Polarity
- Transient interactions

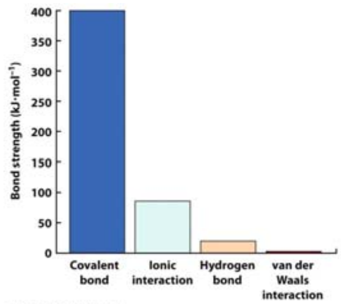


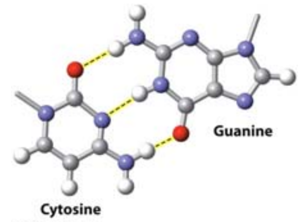


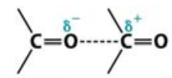


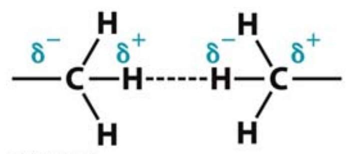
Intermolecular Forces

- Relative strength of IMF
- Permanent dipole
- London dispersion forces



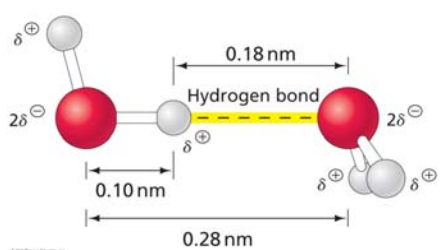


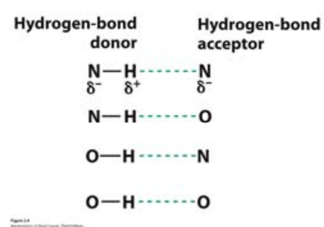




H-bonding

- 1/10 the strength of some covalent bonds
- Donor/acceptor
- ~2.3 H-bonds/ water molecule





Transient Interactions

- Intermediate strength of H-bonds key to function
- Medium for Brownian Motion

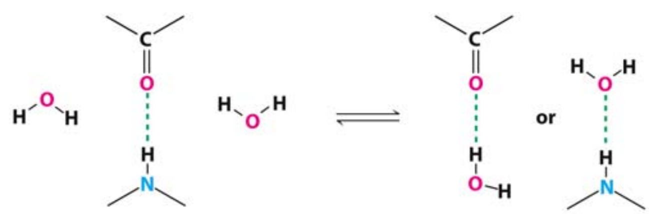


Figure 2.5
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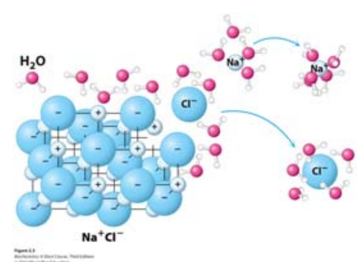
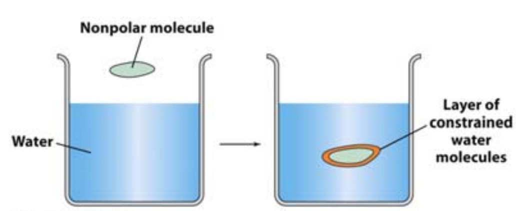
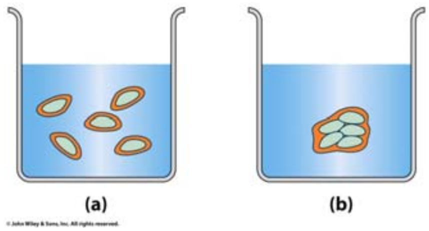
Solvation

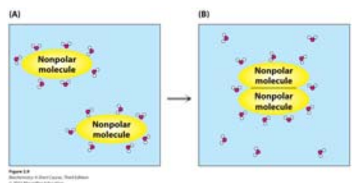
- Dielectric constant
- Solvation shell
- Ionic, polar, and nonpolar compounds





Hydrophobic Effect





- The exclusion of nonpolar substances from aqueous solution
- $\Delta G = \Delta H - T\Delta S$
- Cage-like structure of water molecules minimized upon aggregation
- Powerful structural determination

Structure of Biomolecules

- Increased order in protein
- Decreased order overall
- How?

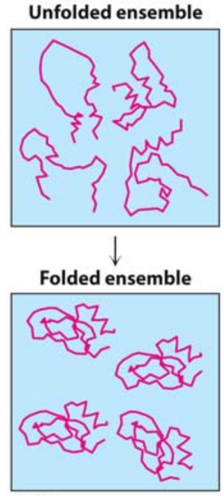


Figure 2.10
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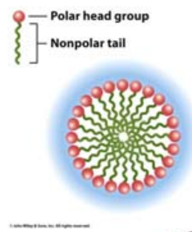
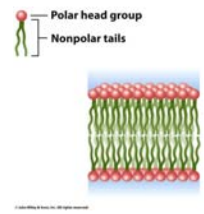
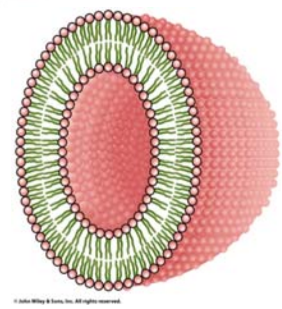
Amphipathic Compounds

- Structures determined by hydrophobic effect
  - Micelles
  - Bilayer
  - Vesicle

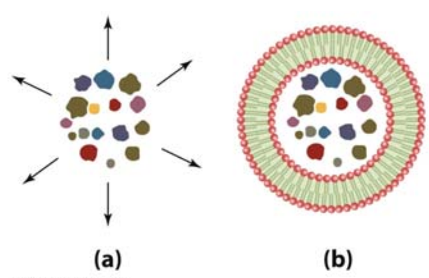


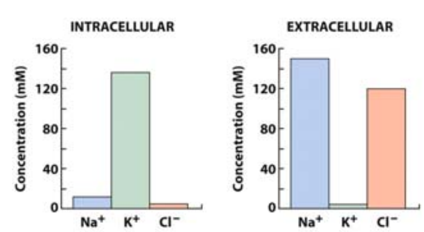




Compartmentalization

- Formation of cells and organelles
- Limits diffusion of molecules unless small and nonpolar (O_2, CO_2)
- Essential for life: don't reach equilibrium!



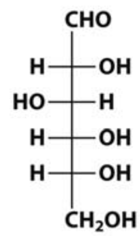


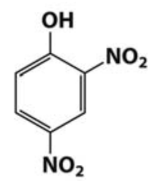
Problem 27

- Which of these substances might be able to cross a bilayer? Explain.

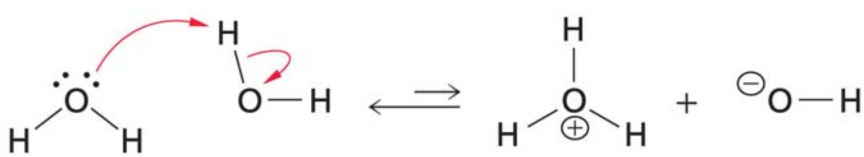
CO_2

Ca^{+2}



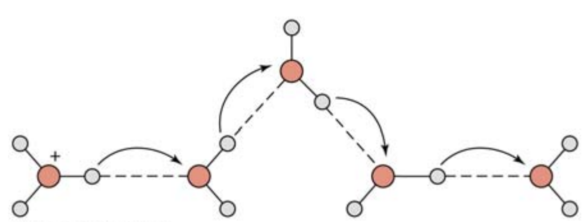


Autoionization of Water



$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$$

Proton jumping: faster than diffusion limit



K_w, The Ion Product of Water

$$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$$

$$K_{eq} = \frac{[H^{\oplus}][OH^{\ominus}]}{H_2O} \qquad K_{eq}[H_2O] = [H^{\oplus}][OH^{\ominus}]$$

$$(1.8 \times 10^{-16}\ M)(55.5\ M) = 1.0 \times 10^{-14}\ M^2 = [H^{\oplus}][OH^{\ominus}]$$

$$K_w = [H^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}\ M^2$$

Reciprocal Relationship

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

pH	$[H^{\oplus}]$ (M)	$[OH^{\ominus}]$ (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}
14	10^{-14}	1

pH of Neutral Water

$$K_w = [H^{\oplus}][OH^{\ominus}] = 1.0 \times 10^{-14}\ M^2$$

$$K_w = [H^{\oplus}]^2 = 1.0 \times 10^{-14}\ M^2$$

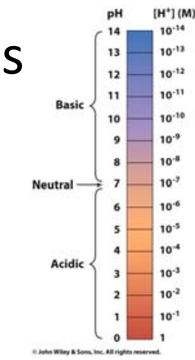
$$[H^{\oplus}] = 1.0 \times 10^{-7}\ M$$

$$pH = -\log[H^{\oplus}] = \log\frac{1}{[H^{\oplus}]}$$

Problem 34

Like all equilibrium constants, the value of K_w is temperature dependent. What is the pH of a neutral solution at 30 ^oC, where $K_w = 1.47 \times 10^{-14}$?

pH of Solutions



- If acid is added to water, the concentration of hydronium increases and pH decreases
- If base is added to water, the concentration of hydronium decreases (ion product of water) and the pH increases
- Addition of MORE acid vs. addition of a STRONGER acid

[TABLE 2-3]

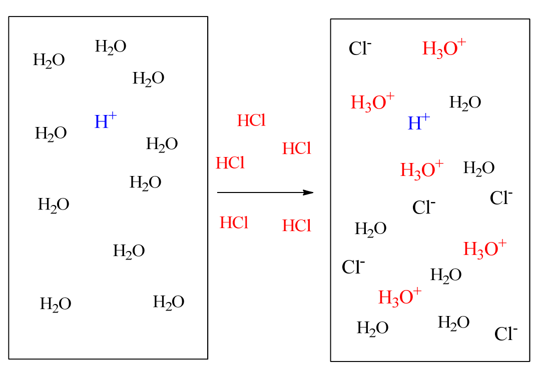
pH Values of Some Biological Fluids

Fluid	pH
Pancreatic juice	7.8–8.0
Blood	7.4
Saliva	6.4–7.0
Urine	5.0–8.0
Gastric juice	1.5–3.0

Strong Acid

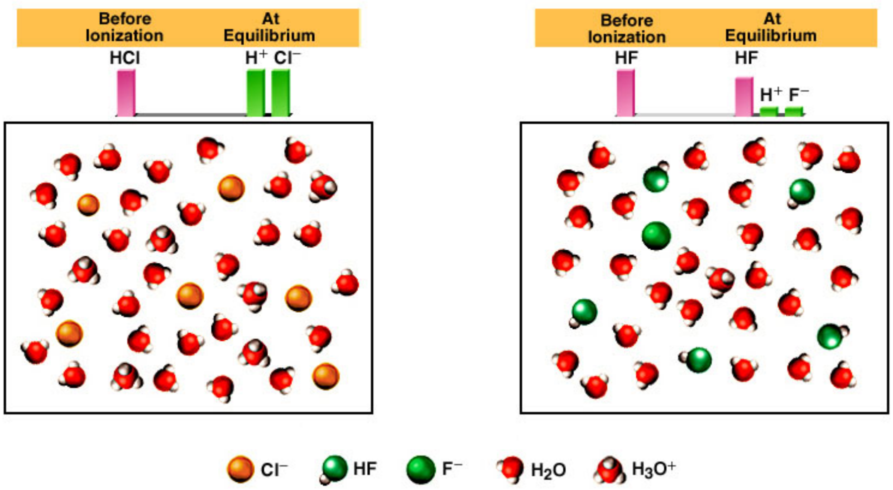
- Complete dissociation
- What is the pH of a 0.01 M HCl solution?
- You add a drop of HCl to make a 1 x 10^{-8} M solution. What is the pH?
- What is your assumption?

$$HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus}$$



Weak Acids

Strong **Weak**



Weak Acid Dissociation Constants

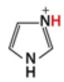
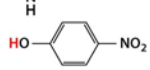
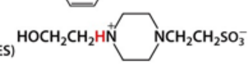
- Weak acids have low [pdts], therefore low K_a
- Low K_a = high pK_a
- Weaker acids have ___________ K_a values and ___________ pK_as

$$CH_3COOH \overset{K_a}{\rightleftharpoons} H^{\oplus} + CH_3COO^{\ominus}$$

Acetic acid (weak acid) — Acetate anion (conjugate base)

$$K_a = \frac{[H^{\oplus}][CH_3COO^{\ominus}]}{[CH_3COOH]}$$

[TABLE 2.4] *pK* Values of Some Acids

Name	Formula [a]	pK
Trifluoroacetic acid	CF_3COOH	0.18
Phosphoric acid	H_3PO_4	2.15[b]
Formic acid	$HCOOH$	3.75
Succinic acid	$HOOCCH_2CH_2COOH$	4.21[b]
Acetic acid	CH_3COOH	4.76
Succinate	$HOOCCH_2CH_2COO^-$	5.64[c]
Thiophenol	C_6H_5SH	6.60
Phosphate	$H_2PO_4^-$	6.82[c]
N-(2-acetamido)-2-amino-ethanesulfonic acid (ACES)	$H_2NCOCH_2\overset{+}{N}H_2CH_2CH_2SO_3^-$	6.90
Imidazole		7.00
p-Nitrophenol		7.24
N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid (HEPES)		7.55
Glycinamide	$^+H_3NCH_2CONH_2$	8.20
Tris(hydroxymethyl)-aminomethane (Tris)	$(HOCH_2)_3C\overset{+}{N}H_3$	8.30
Boric acid	H_3BO_3	9.24
Ammonium ion	NH_4^+ 9.25	
Phenol	C_6H_5OH	9.90
Methylammonium ion	$CH_3NH_3^+$	10.60
Phosphate	HPO_4^{2-}	12.38[d]

[a]The acidic hydrogen is highlighted in red; [b]pK_1; [c]pK_2; [d]pK_3.

Henderson-Hasselbalch

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus} \qquad \log K_a = \log\frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

$$\log K_a = \log[H^{\oplus}] + \log\frac{[A^{\ominus}]}{[HA]}$$

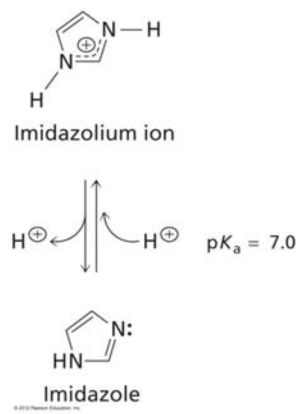
$$-\log[H^{\oplus}] = -\log K_a + \log\frac{[A^{\ominus}]}{[HA]}$$

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

Proton Acceptor

Proton Donor

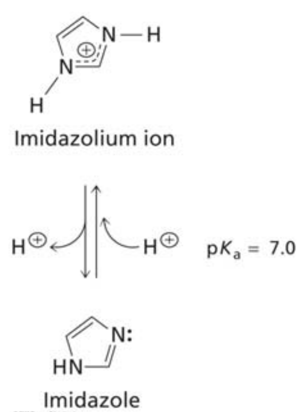
Qualitative Understanding



$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^{\ominus}]}{[\mathrm{HA}]}$$

- Relationship of
  - Solution pH
  - Strength of acid
  - Ratio of CB to CA
- Solve quantitatively, but understand qualitatively

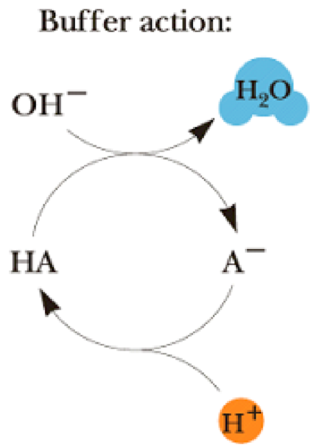
Quantitative Understanding

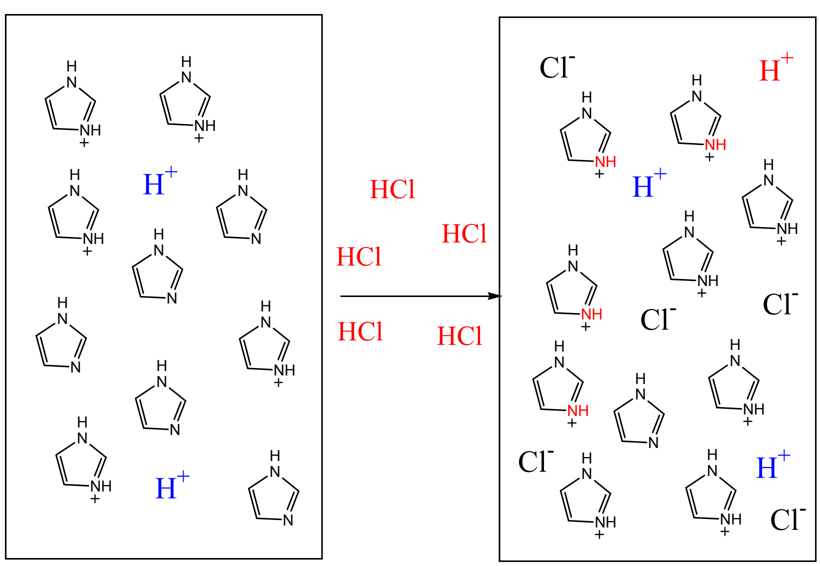


$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^{\ominus}]}{[\mathrm{HA}]}$$

- What percent of molecules in an imidazole buffer are protonated at pH 7.2?

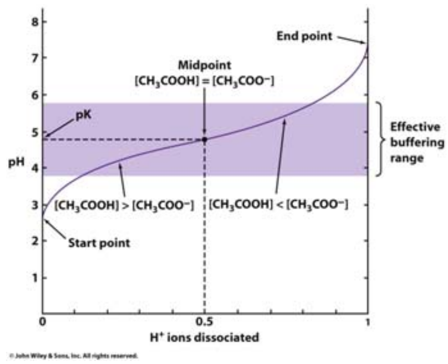
Buffers


Buffer action:
OH⁻
H₂O
HA
A⁻
H⁺


H⁺
H⁺
HCl
HCl
HCl
HCl
HCl
Cl⁻
H⁺
H⁺
Cl⁻
Cl⁻
Cl⁻
H⁺
Cl⁻

Understand Figures

Be able to explain what is happening as you trace the line from left to right in this figure.

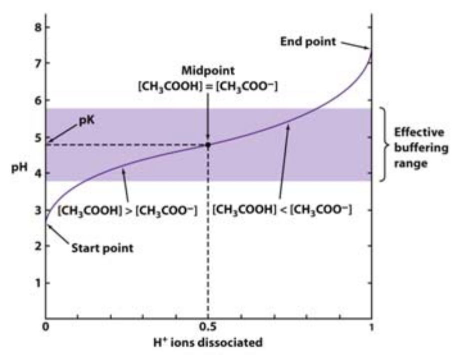


$$pH = pK_a + \log\frac{[A^{\ominus}]}{[HA]}$$

Key Tool in biochemistry: Buffer

Buffer Capacity

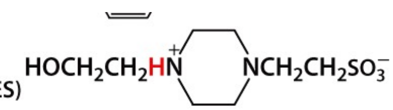
- Depends on pKa of CA/CB mix
- Depends on concentration of CA/CB



Making a Buffer

- **Problem 63**: An experiment requires a HEPES buffer, pH 8.0. Write an equation for dissociation of HEPES. What is its effective buffer range? Describe how you would make 1.0 L of 0.10 M HEPES buffer (MW = 260.3 g/mol) using 6.0 M HCl.

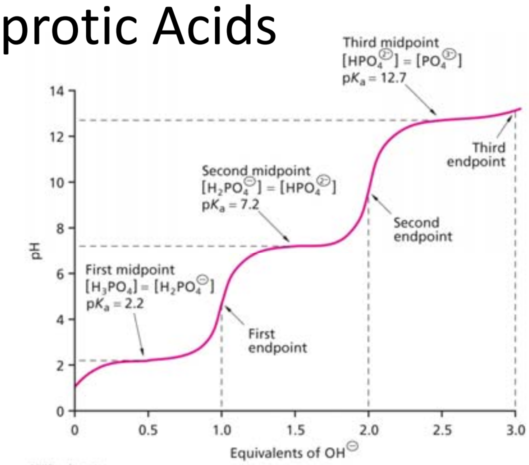
N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid (HEPES)

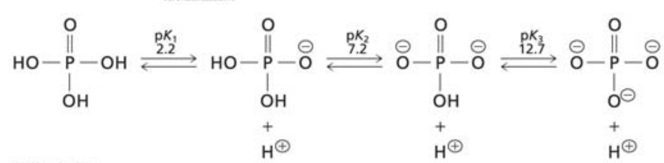


7.55

Polyprotic Acids

- Must be able to match the pKa with the appropriate proton
- Assumptions are legitimate if the pKa values are more than ~3 units from each other





- What is/are the major ionization state(s) for succinic acid at pH 3.2, 4.2, 5.2, and 6.2?

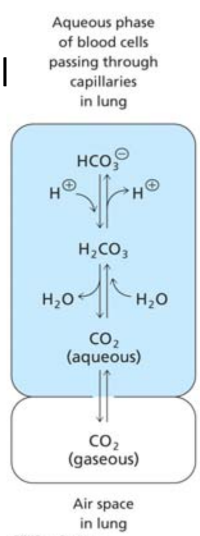
TABLE 2.4 pK Values of Some Acids

Name	Formula*	pK
Trifluoroacetic acid	CF_3COOH	0.18
Phosphoric acid	H_3PO_4	2.15[b]
Formic acid	HCOOH	3.75
Succinic acid	$HOOCCH_2CH_2COOH$	4.21[b]
Acetic acid	CH_3COOH	4.76
Succinate	$HOOCCH_2CH_2COO^-$	5.64[c]
Thiophenol	C_6H_5SH	6.60
Phosphate	$H_2PO_4^-$	6.82[c]
N-(2-acetamido)-2-aminoethanesulfonic acid (ACES)	$H_2NCOCH_2\overset{+}{N}H_2CH_2CH_2SO_3^-$	6.90

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

Blood Buffer

- Physiological pH 7.4
- Closed vs. Open systems
- Acidosis



Normal conditions

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$

Excess acid

$H^+ + HCO_3^- \rightarrow H_2CO_3 \rightleftharpoons H_2O + CO_2$

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightarrow H_2O + CO_2$

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$

Insufficient acid

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \leftarrow H_2O + CO_2$

$H^+ + HCO_3^- \leftarrow H_2CO_3 \rightleftharpoons H_2O + CO_2$

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$

Kidney Function

- Kidneys fight acidosis caused by common metabolic processes
- Reclaims excreted bicarbonate by excreting acid
- Forms new bicarb by CO_2 producing metabolism