

Acid Base Chemistry

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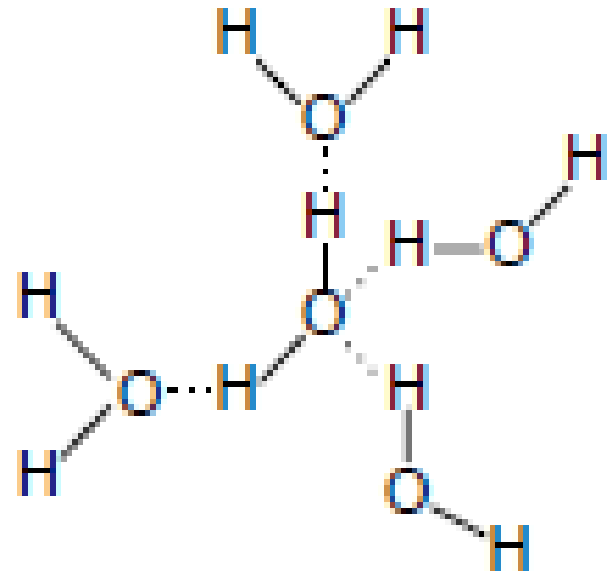
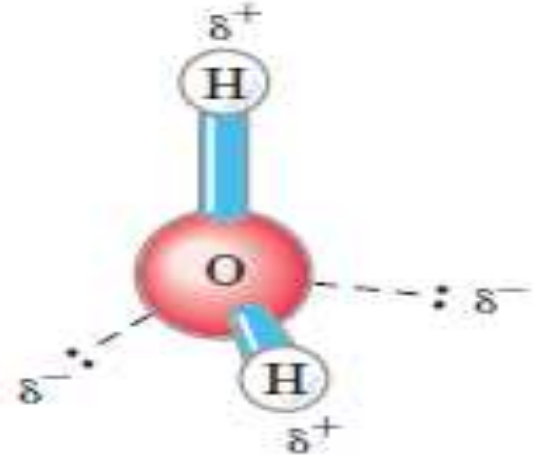
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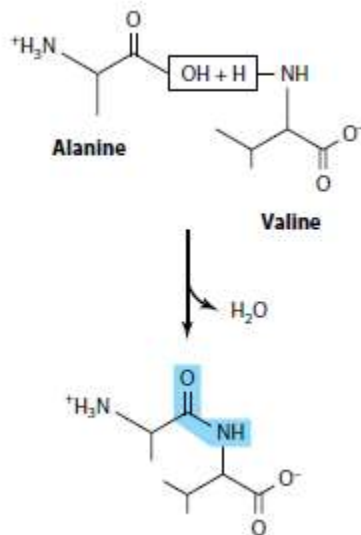
Topics

- Water and chemical properties
- Definitions of acids and bases
- pH scale and Instruments for pH measurement
- Derivation of Henderson-Hasselbach equation
- Relationship between pH, pOH, $[H^+]$, $[OH^-]$, K_w and pKa

Water and chemical properties

- Water is regarded as the predominant chemical component of living organisms.
- Water has the ability to solvate a wide variety of organic and inorganic molecules.
- Water molecules form dipoles.
- Water molecules form hydrogen bonds.





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

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{[10^{-7}][10^{-7}]}{[55.56]}$$

$$= 0.018 \times 10^{-14} = 1.8 \times 10^{-16} \text{ mol/L}$$

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.8 \times 10^{-16} \text{ mol/L}$$

$$\begin{aligned} K_w &= (K)[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] \\ &= (1.8 \times 10^{-16} \text{ mol/L}) (55.56 \text{ mol/L}) \\ &= 1.00 \times 10^{-14} (\text{mol/L})^2 \end{aligned}$$

pH

- **pH IS THE NEGATIVE LOG OF THE HYDROGEN ION CONCENTRATION**
- The term **pH** was introduced in 1909 by Sørensen, who defined pH as the negative log of the hydrogen ion concentration:
 - $\text{pH} = -\log [\text{H}^+]$
 - For example, for pure water at 25°C,
 $-\log [\text{H}^+] = -\log [10^{-7}] = -[-7] = 7$
- Acids are **proton donors** and bases are **proton acceptors**.
- **Strong acids** (eg, HCl or H₂SO₄) completely dissociate into anions and cations even in strongly acidic solutions (low pH).
- **Weak acids** dissociate only partially in acidic solutions.
- Similarly, **strong bases** (eg, KOH or NaOH) — but not **weak bases** (eg, Ca[OH]₂) — are completely dissociated at high pH.

pH Scale

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

*The expression pOH is sometimes used to describe the basicity, or OH^- concentration, of a solution; pOH is defined by the expression $pOH = -\log [OH^-]$, which is analogous to the expression for pH. Note that in all cases, $pH + pOH = 14$.

Example 1: What is the pH of a solution whose hydrogen ion concentration is 3.2×10^{-4} mol/L?

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log (3.2 \times 10^{-4})$$

$$= -\log (3.2) - \log (10^{-4})$$

$$= -0.5 + 4.0$$

$$= 3.5$$

Example 2: What is the pH of a solution whose hydroxide ion concentration is $4.0 \times 10^{-4} \text{ mol/L}$?

Solution: We first define a quantity **pOH** that is equal to $-\log [\text{OH}^-]$ and that may be derived from the definition of K_w :

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

Therefore:

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

or

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

To solve the problem by this approach:

$$[\text{OH}^-] = 4.0 \times 10^{-4}$$

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

$$= -\log (4.0 \times 10^{-4})$$

$$= -\log (4.0) - \log (10^{-4})$$

$$= -0.60 + 4.0$$

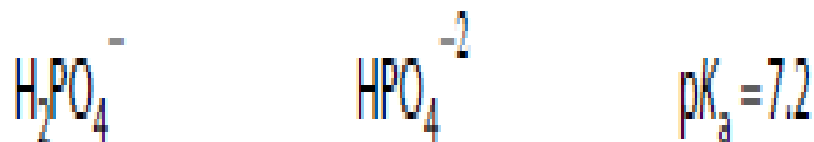
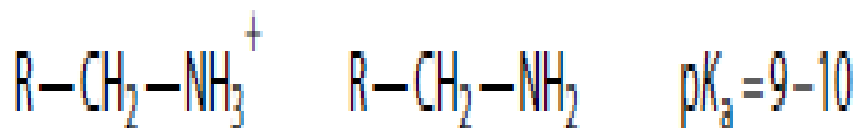
$$= 3.4$$

Now:

$$\text{pH} = 14 - \text{pOH} = 14 - 3.4$$

$$= 10.6$$

Functional Groups That Are Weak Acids Have Great Physiologic Significance



$$K_a = \frac{[R-COO^-][H^+]}{[R-COOH]}$$



$$K_a = \frac{[R-NH_2][H^+]}{[R-NH_3^+]}$$



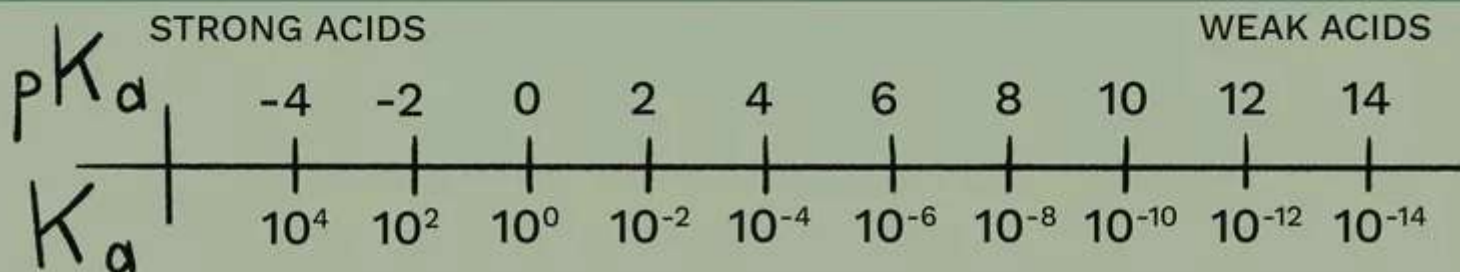
The pKa is the pH at which the concentration of the acid $R-NH_3^+$ equals that of the base $R-NH_2$.

What Is pK_a in Chemistry?

The pK_a value is the negative base-10 logarithm of the acid dissociation constant (K_a) of a solution.

$$pK_a = -\log_{10} K_a$$

The smaller the value of pK_a , the stronger the acid.



- pK_a is the negative base-10 logarithm of the acid dissociation constant(K_a) of a solution.
 $pK_a = -\log_{10} K_a$
- **The lower the pK_a value, the stronger the acid.** For example, the pK_a of acetic acid is 4.8, while the pK_a of lactic acid is 3.8. Using the pK_a values, one can see lactic acid is a stronger acid than acetic acid.
- The reason pK_a is used is because it describes acid dissociation using small decimal numbers. The same type of information may be obtained from K_a values, but they are typically extremely small numbers given in scientific notation that are hard for most people to understand.

pKa and Buffer Capacity

In addition to using pKa to gauge the strength of an acid, it may be used to select buffers. This is possible because of the relationship between pKa and pH:

$$\text{pH} = \text{pK}_a + \log_{10}([\text{A}^-]/[\text{AH}])$$

Where the square brackets are used to indicate the concentrations of the acid and its conjugate base.

The equation may be rewritten as:

$$\text{K}_a/[\text{H}^+] = [\text{A}^-]/[\text{AH}]$$

This shows that pKa and pH are equal when half of the acid has dissociated. The buffering capacity of a species or its ability to maintain pH of a solution is highest when the pKa and pH values are close. So, when selecting a buffer, the best choice is the one that has a pKa value close to the target pH of the chemical solution.

Henderson-Hasselbach Equation

$$\text{pH} = \text{pK}_a + \log \frac{\text{Base}[\text{A}^-; \text{B}]}{\text{Acid}[\text{HA}; \text{BH}^+]}$$

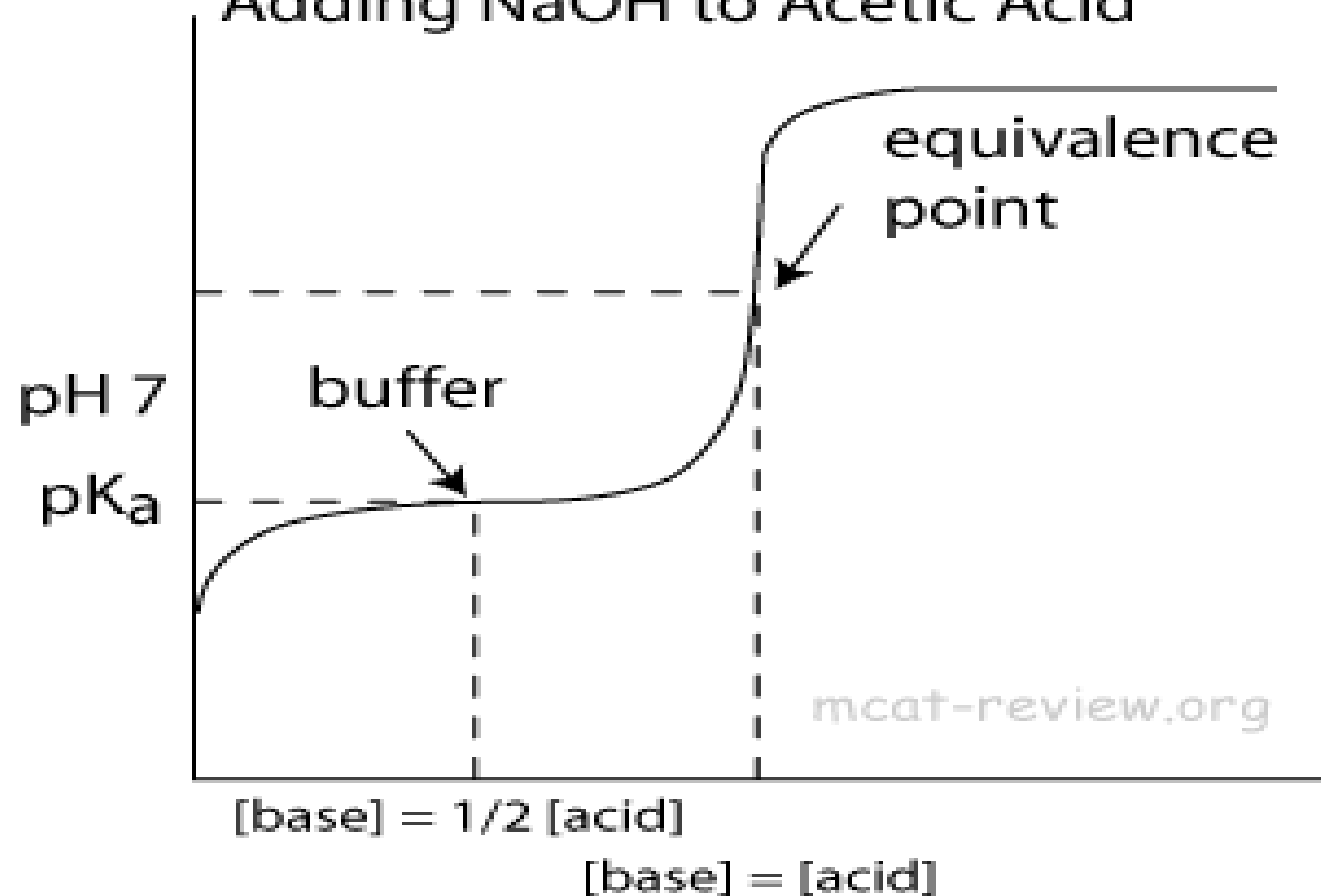
weak acids = $[\text{HA} \leftrightarrow \text{H}^+ + \text{A}^-]$ Acid is a proton donor

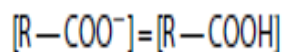
weak bases = $[\text{B} + \text{H}^+ \leftrightarrow \text{BH}^+]$ Base is a proton acceptor

H-H equation is used to calculate the percent ionization of a drug in cellular compartments of different pH.

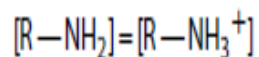
Understanding how changes in pH alter the ionization of drugs is very important since unionized drugs cross membranes.

Adding NaOH to Acetic Acid





or when



then

$$K_a = [H^+]$$

Thus, when the associated (protonated) and dissociated (conjugate base) species are present at equal concentrations, the prevailing hydrogen ion concentration $[H^+]$ is numerically equal to the dissociation constant, K_a .

ie, the pK_a of an acid group is the pH at which the protonated and unprotonated species are present at equal concentrations.

The pK_a for an acid may be determined by adding 0.5 equivalent of alkali per equivalent of acid. The resulting pH will be the pK_a of the acid.

The Henderson-Hasselbalch Equation Describes the Behavior of Weak Acids & Buffers

The Henderson-Hasselbalch equation is derived below.
A weak acid, HA, ionizes as follows:



The equilibrium constant for this dissociation is

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

Cross-multiplication gives

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

Divide both sides by $[\text{A}^-]$:

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

Take the log of both sides:

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

Multiply through by -1 :

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

Substitute pH and $\text{p}K_a$ for $-\log [\text{H}^+]$ and $-\log K_a$, respectively; then:

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

Inversion of the last term removes the minus sign and gives the Henderson-Hasselbalch equation:

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

The Henderson-Hasselbalch equation has great predictive value in protonic equilibria. For example,

(1) When an acid is exactly half-neutralized, $[\text{A}^-] = [\text{HA}]$. Under these conditions,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a + \log \frac{1}{1} = \text{p}K_a + 0$$

Therefore, at half-neutralization, $\text{pH} = \text{p}K_a$.

(2) When the ratio $[\text{A}^-]/[\text{HA}] = 100:1$,

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \\ \text{pH} &= \text{p}K_a + \log 100/1 = \text{p}K_a + 2 \end{aligned}$$

(3) When the ratio $[\text{A}^-]/[\text{HA}] = 1:10$,

$$\text{pH} = \text{p}K_a + \log 1/10 = \text{p}K_a + (-1)$$

Buffers and Buffer System

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Topics

- Bicarbonate and Non-bicarbonate buffer systems

Solutions of Weak Acids & Their Salts

Buffer Changes in pH

- Solutions of weak acids or bases and their conjugates exhibit buffering, the ability to resist a change in pH following addition of strong acid or base. Since many metabolic reactions are accompanied by the release or uptake of protons, most intracellular reactions are buffered.

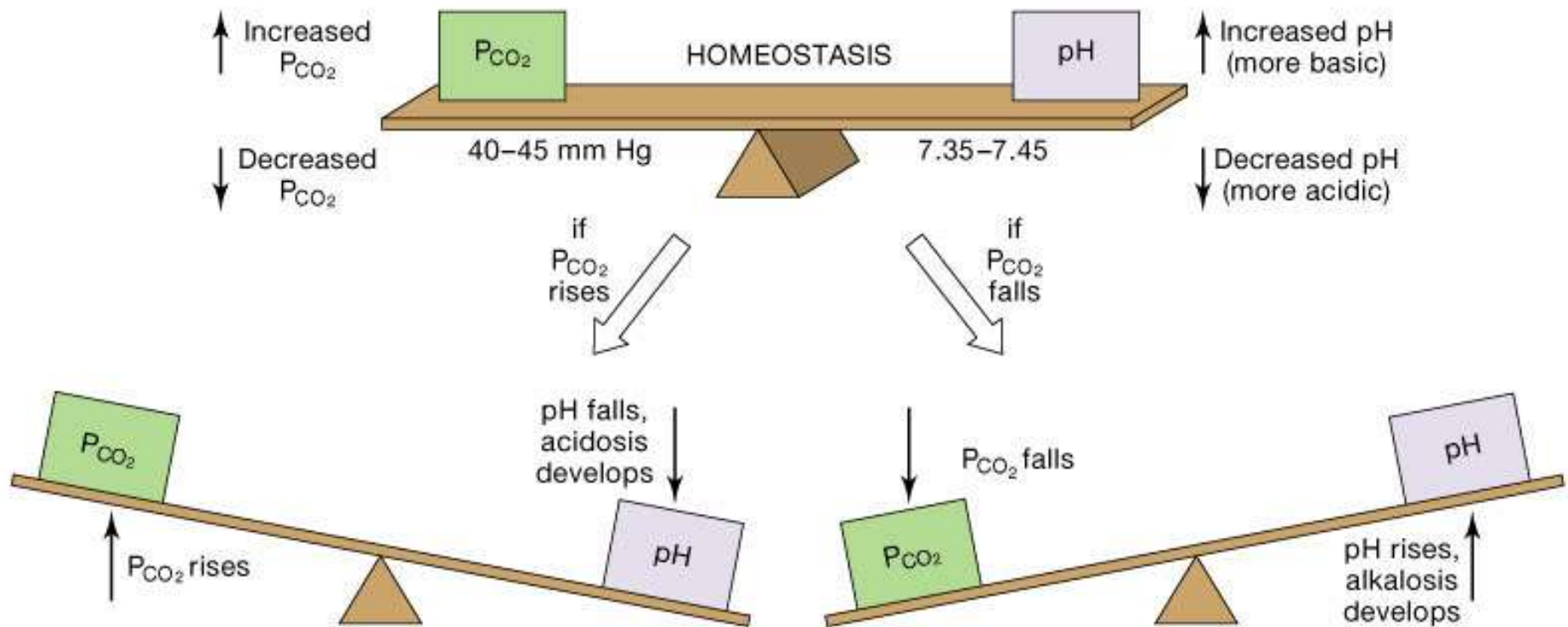
Mechanisms of pH control

- Buffer system consists of a weak acid and its anion
- Three major buffering systems:
 - Protein buffer system
 - Amino acid
 - Hemoglobin buffer system
 - H^+ are buffered by hemoglobin
 - Carbonic acid-bicarbonate
 - Buffers changes caused by organic and fixed acids

Mechanisms of pH control

- Three major buffering systems (continued):
 - Minor buffering system
 - Phosphate
 - Buffer pH in the ICF
 - Operates in the internal fluid of all cells. It consists of dihydrogen phosphate ions (as the hydrogen ion donor or acid) and hydrogen phosphate ions as the hydrogen ion acceptor or base.

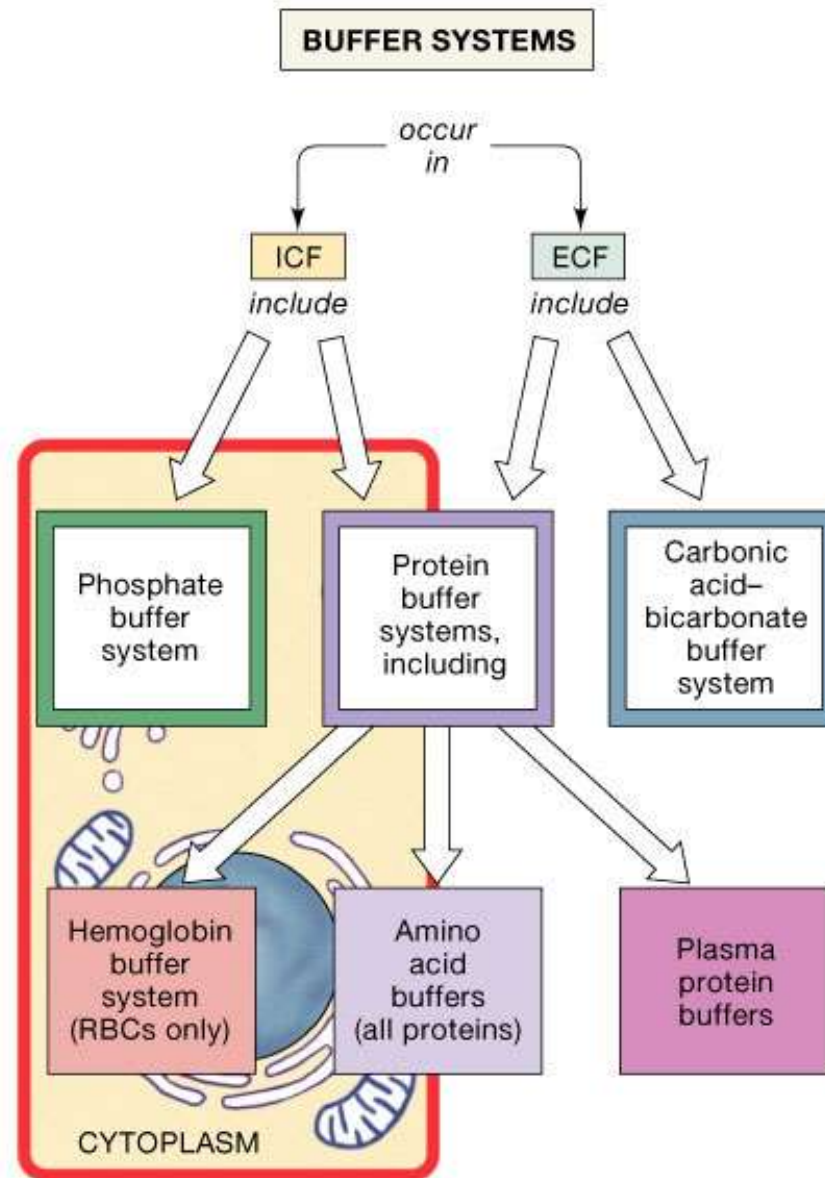
The Basic Relationship between P_{CO_2} and Plasma pH



PLAY

Animation: Relationship Between P_{CO_2} and Plasma pH

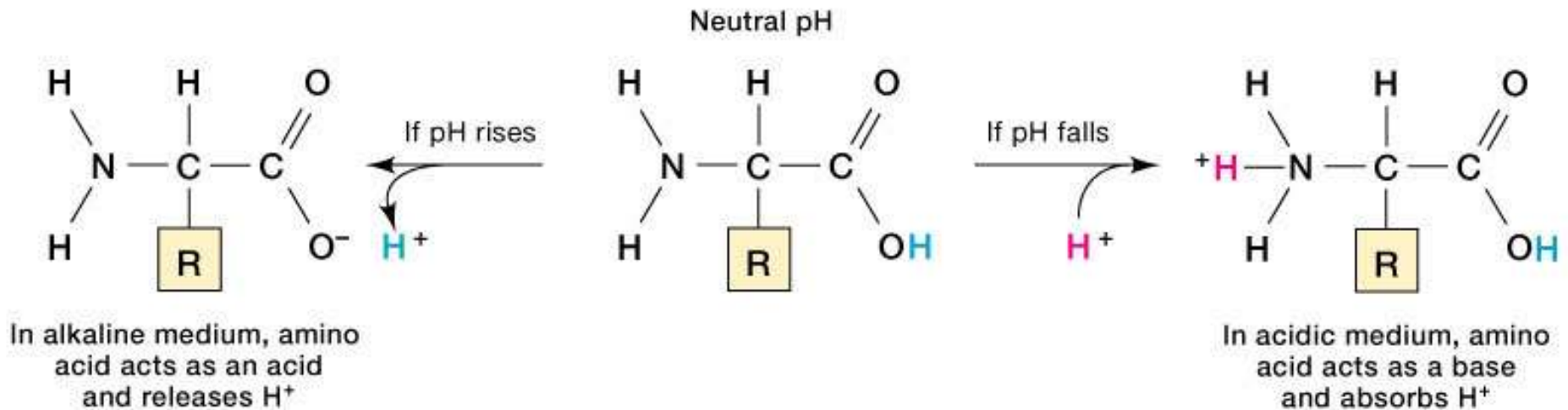
Buffer Systems in Body Fluids



Protein buffer system

- If pH climbs, the carboxyl group of amino acid acts as a weak acid
- If the pH drops, the amino group acts as a weak base
- Hemoglobin buffer system
 - Prevents pH changes when P_{CO_2} is rising or falling

Amino Acid Buffers



Carbonic Acid-Bicarbonate Buffering System

- Carbonic acid-bicarbonate buffer system
 - $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$
- Has the following limitations:
 - Cannot protect the ECF from pH changes due to increased or depressed CO_2 levels
 - Only functions when respiratory system and control centers are working normally
 - It is limited by availability of bicarbonate ions (bicarbonate reserve)

- As with any buffer system the pH is balanced by the presence of both a weak acid (H_2CO_3) and its conjugate base (HCO_3^-) so that any excess acid or base introduced to the system is neutralized.
- Failure of the bicarbonate buffer system to function normally results in acid-base imbalance (irregular pH) in the blood.

The Carbonic Acid-Bicarbonate Buffer System

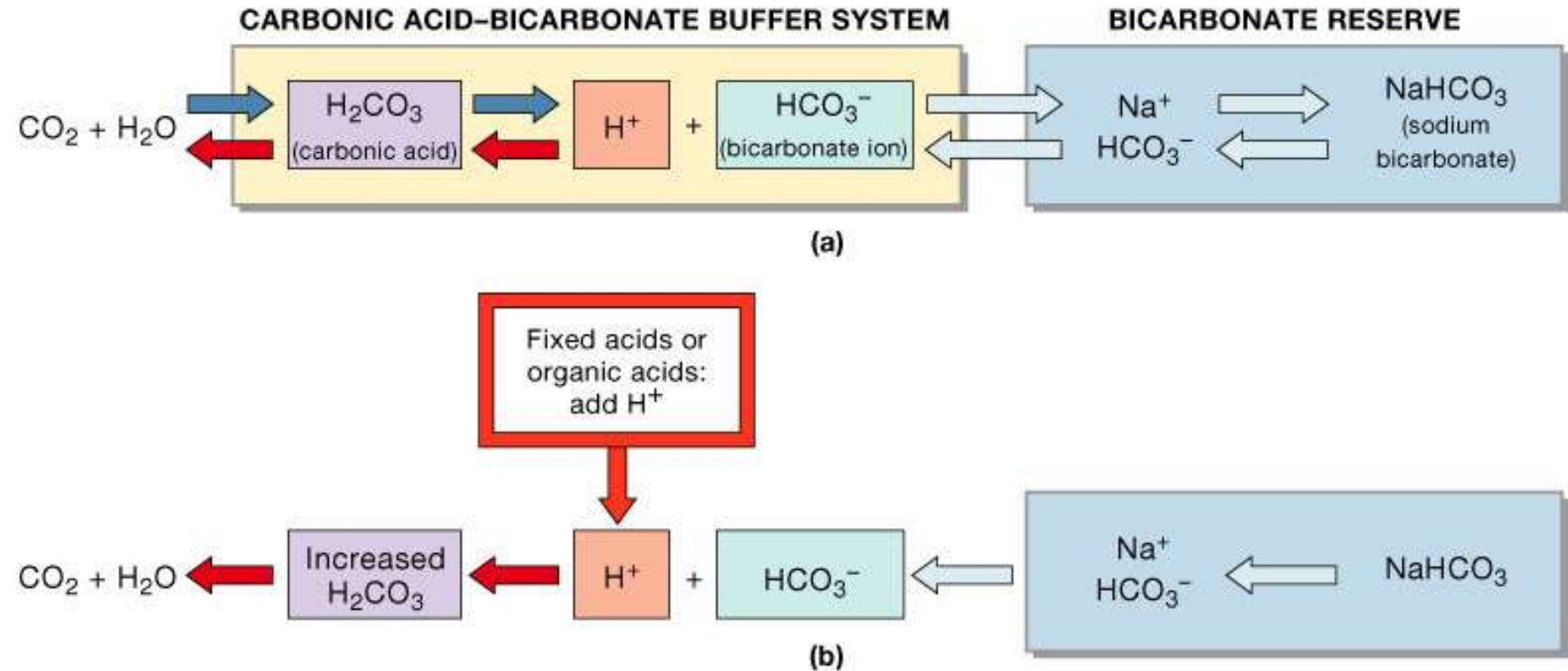


Figure 27.9a, b

Maintenance of acid-base balance

- Lungs help regulate pH through carbonic acid - bicarbonate buffer system
 - Changing respiratory rates changes P_{CO_2}
 - Respiratory compensation
- Kidneys help regulate pH through renal compensation. They release H^+ into urine, reabsorbing HCO_3^- into the blood plasma.
- Cellular respiration produces CO_2 , which is removed rapidly from the system through hydration to produce bicarbonate ion.
- The bicarbonate ion present in the blood plasma is transported to the lungs, where it is dehydrated back into CO_2 and released during exhalation.

Regulation of pH

- Using the Henderson-Hasselbalch equation, in order to maintain a normal blood pH of 7.4 (where the pKa of carbonic acid is 6.1), a ratio of 20:1 bicarbonate ion/carbonic acid must be maintained.
- According to Le Chatelier's principle, the release of CO₂ from the lungs will push the reaction above to the left, causing carbonic anhydrase to form more CO₂ until all excess proton has been removed.