

# Dissociation of Acids, pH, Buffer Systems, Henderson-Hasselbalch Equation

Acid-Base Chemistry

- What is a **buffer?**

The diagram shows two beakers representing a buffered solution. In the first beaker, labeled "Solution containing  $\text{H}_2\text{CO}_3$ ;  $\text{HCO}_3^-$  buffer", there are three red circles representing  $\text{H}_2\text{CO}_3$  molecules and several blue and yellow circles representing  $\text{HCO}_3^-$  and  $\text{Na}^+$  ions. An arrow labeled "Addition of 3 HCl to buffered solution" points to the second beaker. In the second beaker, labeled "1 free  $\text{H}^+$  present", the red circles are now  $\text{H}_3\text{O}^+$  ions, and the blue and yellow circles remain as  $\text{HCO}_3^-$  and  $\text{Na}^+$ . Labels include "© 2001 Brooks/Cole - Thomson Learning", "Sherwood Figure 15-8", and "HCl".



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# Behavior of Acids/Bases

The theory of acids/bases has changed over time due to research and experimentation-

- Arrhenius (oldest)
- Bronsted-Lowrey
- Lewis acids/bases (newest)

# Arrhenius Definition - 1887

- Acids produce hydrogen cations ( $\text{H}^+$ ) or hydronium ions ( $\text{H}_3\text{O}^+$ ) when dissolved in water ( $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ )
- Bases produce hydroxide anions ( $\text{OH}^-$ ) when dissolved in water ( $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$ )

# Brønsted-Lowry - 1923

- A broader definition than Arrhenius
- Acid is hydrogen-ion donor ( $H^+$  or proton); base is hydrogen-ion acceptor.
- Acids and bases always come in pairs.
- HCl is an acid. – When it dissolves in water, it gives its proton to water.  $HCl(g) + H_2O(l) \leftrightarrow H_3O^+(aq) + Cl^-(aq)$ . Here, Water is a base; makes hydronium ion.
- Ammonia can be explained as a base. Ammonia is the hydrogen ion acceptor (base), and water is the hydrogen ion donor (acid). This causes the  $OH^-$  concentration to be greater than in pure water, and the ammonia solution is basic.  $NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

# **Conjugate Acid/ Conjugate Base**

- A “**conjugate base**” is the charged particle of the original acid, after it **donates its hydrogen ion**.
- A “**conjugate acid**” is the charged particle formed when the original base **gains a hydrogen ion**.
- Thus, a conjugate acid-base pair is related by the loss or gain of a single hydrogen ion.

# Acids and Bases come in Pairs

- General equation is:  $\text{HA(aq)} + \text{H}_2\text{O(l)} \leftrightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{A}^- (\text{aq})$   
Acid + Base  $\leftrightarrow$  Conjugate acid + Conjugate base
- $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$   
Base    Acid              C.A.      C.B.
- $\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$   
Acid    Base              C.A.      C.B.
- Some compounds can act as both proton donor and proton acceptor (act as **both** an acid and base) and these compounds are known as **Ampholytes** or **Amphoteric** (Water & Amino acids ).

# Lewis Acids and Bases (1875-1946)

- Gilbert Lewis focused on the donation or acceptance of a pair of electrons during a reaction.
- **Lewis Acid** - electron pair acceptor
- **Lewis Base** - electron pair donor
- On ionization, an **acid donates a proton and a base (which is capable of accepting a proton)**. This base is known as a **Conjugate base**.

# Acids & Bases

**Acid :** yields H<sup>+</sup> ions ( HCl → H<sup>+</sup> + Cl<sup>-</sup> )

**Base :** combines with H<sup>+</sup> ions ( Na<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> ) ← combines with H<sup>+</sup>

HCl ( strong acid ) → H<sup>+</sup> + Cl<sup>-</sup> ( weak base )



H<sub>2</sub>CO<sub>3</sub> ( weak acid ) → H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> ( strong base )

- **Acid** is a substance whose dissociation in water releases hydrogen ions (H<sup>+</sup>)
- Addition of an acid to a solution, increases concentration of free H<sup>+</sup> in the solution.
- Produces more acidic solution & decrease in pH.



- A **base** releases hydroxyl ions (OH<sup>-</sup>) in aqueous solution & decreases its H<sup>+</sup> concentration by accepting or by binding with free H<sup>+</sup>.
- This results in increase in pH of the solution. The OH<sup>-</sup>, accepts H<sup>+</sup> & results in the formation of water.



- The term **Alkali** is reserved for those compounds that yield OH<sup>-</sup> ions on dissociation



# Acids and Bases

pH less than 7

taste sour

react with bases

proton ( $H^{1+}$ ) donor

turn litmus **red**

lots of  $H^{1+}/H_3O^{1+}$

react w/metals



**litmus paper**

pH greater than 7

taste bitter

react with acids

proton ( $H^{1+}$ ) acceptor

turn litmus **blue**

lots of  $OH^{1-}$

don't react w/metals

Both are electrolytes. (they conduct electricity in soln)

# Concentration vs. Strength

- The words **concentrated** and **dilute** tell how much of an acid or base is dissolved in solution - refers to the number of moles of acid or base in a given volume.
- The words **strong** and **weak** refer to the extent of ionization of an acid or base. Strong = 80% - 100% ionization.

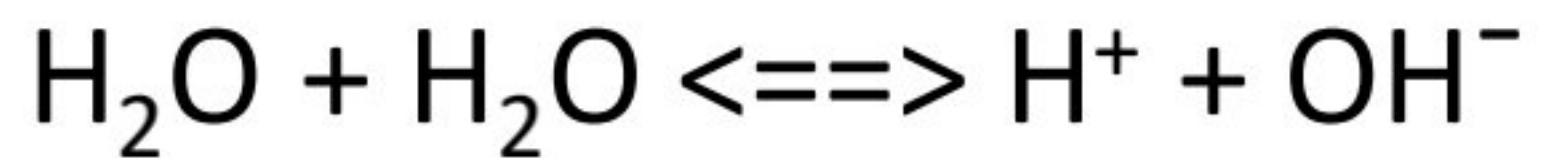
Weak = 10% - 30 % ionization

- HCl (Hydrochloric Acid) is a strong acid - it completely ionizes (100%) in water and carbonic acid & acetic acid are weak acids.

# pH

- The  $\text{H}^+$  ion concentration of most of the biological solutions is very low and is in the range of  $10^{-1}$  to  $10^{-14}$  gram ions/L, which is very difficult to measure and express in conventional method of expression. Hence, **Sorenson** in 1909 introduced the term pH, to express **the hydrogen ion concentration in a logarithmic scale, which is defined as  $\text{pH} = -\log \text{ of } [\text{H}^+]$  or  $\log 1 / [\text{H}^+]$ .**
- According to this the  $[\text{H}^+]$  concentration of  $10^{-8}$  g /L will be pH 8.0. The 'pH' denotes '**negative logarithm of the hydrogen ion concentration  $[\text{H}^+]$** '. 'P' also stands for power. pH is the abbreviation of '**power of hydrogen**'
- The pH scale is the useful way of expressing acidity, which in turn dependent on  $[\text{H}^+]$ . pH is generally in the range of **0 - 14**, as **the dissociation constant ( $K_w$ ) of water at  $25^\circ\text{C}$  is  $10^{-14}$** .
- An acidic solution has a pH below 7 and a basic solution has a pH above 7. Pure water is neither acidic nor basic and is said to be neutral  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  M
- **pH is inversely related to hydrogen ion concentration.** That is lower the pH the higher the  $\text{H}^+$  ion concentration.
- **The pH scale is logarithmic (exponential) not arithmetic (linear).** This means that when a solution changes from pH 7 to pH 6, the  $\text{H}^+$  ion concentration increases by 10 fold. When it goes from pH 7 to pH 5 it increases by 100 fold. The pH of water is 7.0 that means water contains  $1 \times 10^{-7}$  g of  $\text{H}^+$  ions/L.

# pH



By applying the Law of mass action for  
the dissociation of water-

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

In Pure Water ( Neutral)

$$\text{Dissociation Constant } K_w = [\text{H}^+] [\text{OH}^-]$$

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

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = 7$$

$$\text{pOH} = -\log_{10} [\text{H}^+] = 7$$

**TABLE 2-6 The pH Scale**

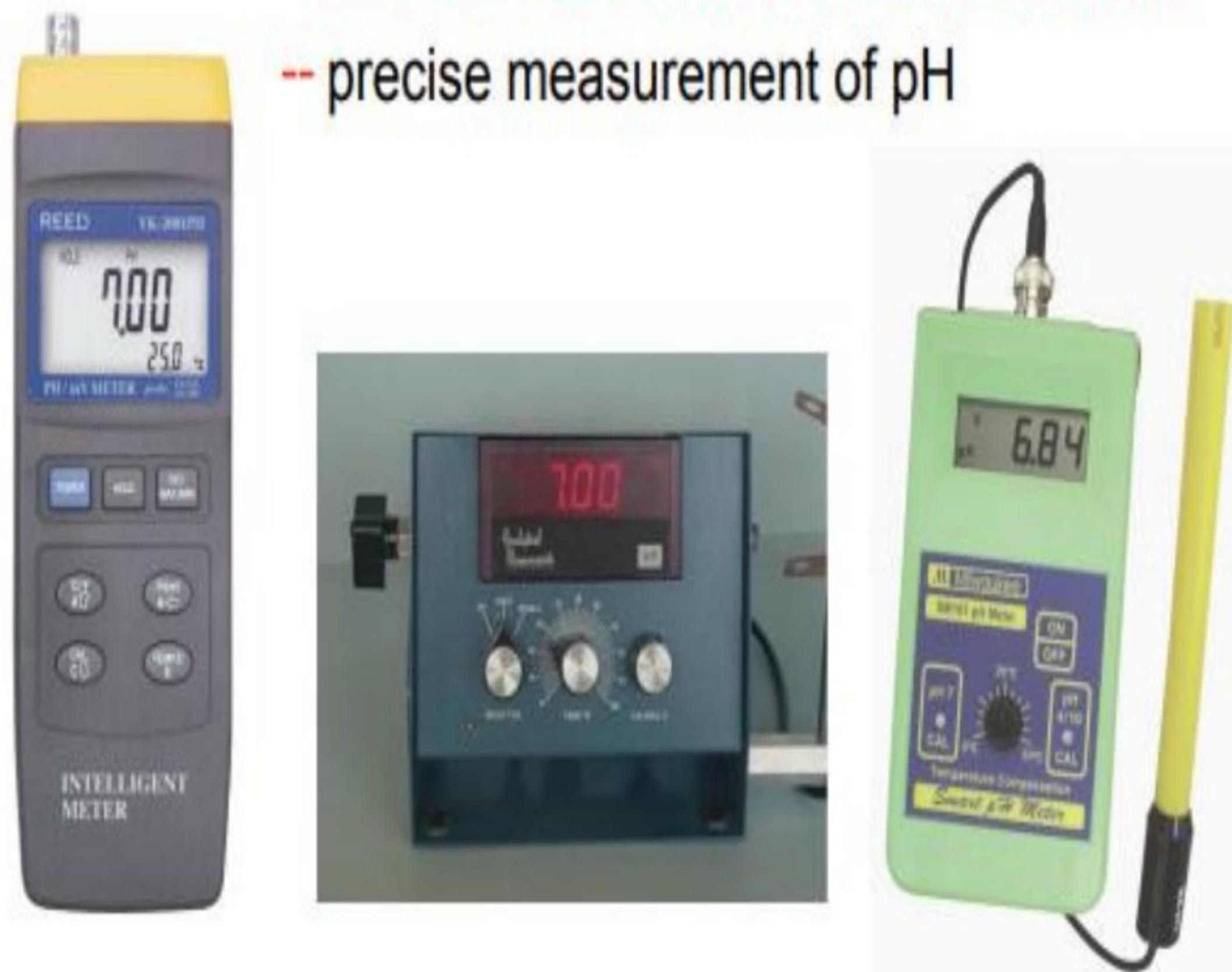
[H <sup>+</sup> ] (M)	pH	[OH <sup>-</sup> ] (M)	pOH*
10 <sup>0</sup> (1)	0	10 <sup>-14</sup>	14
10 <sup>-1</sup>	1	10 <sup>-13</sup>	13
10 <sup>-2</sup>	2	10 <sup>-12</sup>	12
10 <sup>-3</sup>	3	10 <sup>-11</sup>	11
10 <sup>-4</sup>	4	10 <sup>-10</sup>	10
10 <sup>-5</sup>	5	10 <sup>-9</sup>	9
10 <sup>-6</sup>	6	10 <sup>-8</sup>	8
10 <sup>-7</sup>	7	10 <sup>-7</sup>	7
10 <sup>-8</sup>	8	10 <sup>-6</sup>	6
10 <sup>-9</sup>	9	10 <sup>-5</sup>	5
10 <sup>-10</sup>	10	10 <sup>-4</sup>	4
10 <sup>-11</sup>	11	10 <sup>-3</sup>	3
10 <sup>-12</sup>	12	10 <sup>-2</sup>	2
10 <sup>-13</sup>	13	10 <sup>-1</sup>	1
10 <sup>-14</sup>	14	10 <sup>0</sup> (1)	0

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

# Measuring pH

The pH of an aqueous solution can be approximately measured using various indicator dyes, including litmus, phenolphthalein and phenol red, which undergo colour changes as a proton dissociate from the dye molecule.

- pH meter -- measures small voltages in solutions
- calibrated to convert voltages into pH
- precise measurement of pH



**Indicators** → chemicals that change color, depending on the pH

Two examples, out of many:

litmus.....

red in acid,  
blue in base



phenolphthalein.....

clear in acid,  
pink in base



litmus paper  
phenolphthalein }

Basically, pH < 7 or pH > 7.

pH paper -- contains a mixture of various indicators

- each type of paper measures a range of pH
- pH anywhere from 0 to 14



universal indicator -- is a mixture of several indicators

-- pH 4 to 10

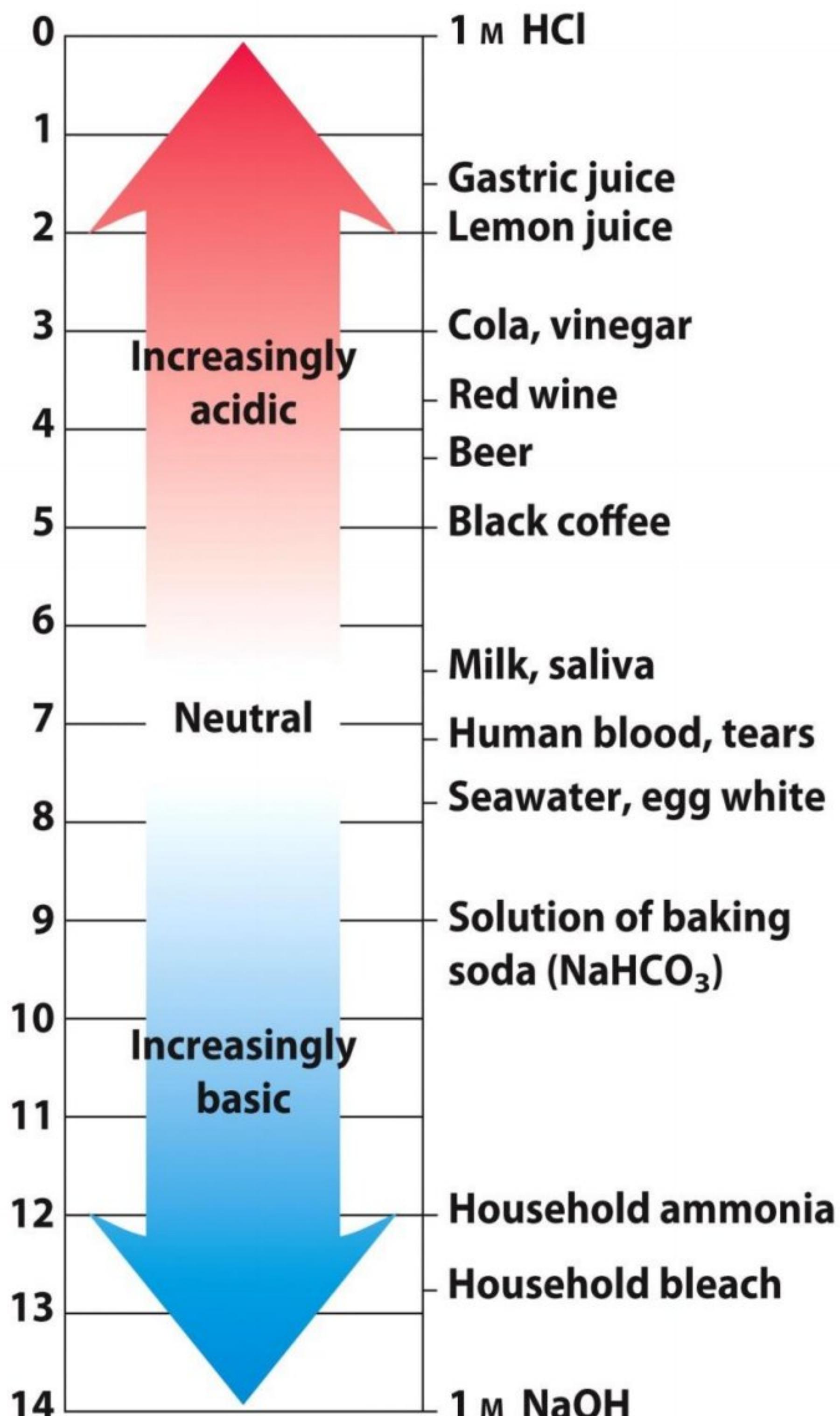
← 4 5 6 7 8 9 10 →

R O Y G B I V



# pH Values of Some Common Liquids

- The **biochemical processes** such as transport of oxygen in the blood, the catalysis of reactions by enzymes and the generation of metabolic energy are strongly affected by the concentration of H<sup>+</sup> ion. Many biological reactions are dependent on the charge on the molecules (+ ve or -ve charge)
- The **pH of biological solutions is carefully controlled because pH strongly affects the structure and activity of biological macromolecules, e.g., enzymes.**
- Measurement of pH sometimes used in the diagnosis of diseases. The normal pH of human plasma is 7.4, which is referred to as **physiological pH**. The blood of patients suffering from certain diseases such as **diabetes can have a lower pH**, a condition called **acidosis**. The condition in which the pH of the **blood is higher than 7** is called **alkalosis**.



# pH of some Important Biological Fluids

Fluid	pH
Pancreatic juice	7.5-8.0
Blood Plasma (or whole blood)	7.35-7.45
Cerebrospinal fluid	7.2-7.4
Tears	7.2-7.4
Interstitial fluid	7.2-7.4
Human milk	7.2-7.4
Saliva	6.4-7.0
Intra-cellular fluid (cytosol)	6.5-6.9
Gastric juice	1.5-3.0
Urine	5.0-7.5

**Buffers : solutions resists the change in pH on addition of acid or base**

**Acidic buffer : weak acid + its salt with strong base**  
eg  $\text{H}_2\text{CO}_3$  (weak acid) +  $\text{NaHCO}_3^-$  (strong base)

**Basic /Alkaline buffer : weak base + its salt with strong acid**  
eg  $\text{NH}_4\text{OH}$  +  $\text{NH}_4\text{Cl}$

- A buffer solution is one that resists pH change on the addition of a small quantity of acid or alkali.
- Such solutions are used in biochemical experiments, where the pH is to be accurately controlled.
- A buffer may be defined as a solution of a weak acid & its salt with a strong base. A buffer solution consists of a weak acid and its salt, the conjugate base (the proton acceptor) e.g. acetic acid and sodium acetate or a weak base and its salts e.g. ammonium hydroxide and ammonium chloride.
- During buffering strong acid or base is replaced by a weaker one, with a consequent reduction in the number of free hydrogen ( $\text{H}^+$ ) or hydroxyl ion ( $\text{OH}^-$ ).

# **Buffering Capacity**

- The efficiency of a buffer in maintaining a constant pH on the addition of acid or base is referred to as **Buffering capacity**. It is the number of gram equivalents of either hydrogen ion or hydroxyl ion required to change the pH of 1L of 1M solutions by 1 unit.
- It mostly depends on the concentration of buffer components. The maximum buffering capacity is usually achieved by keeping the same concentration of the salt as well as the acid.

# Buffers

- First line of defence (> 50 – 100 mEq/day)
- Two most common chemical buffer groups:
  - ❖ **Bicarbonate**
  - ❖ **Non-bicarbonate (Hb, protein, phosphate)**
- Blood buffer systems act instantaneously
- Regulate pH by binding or releasing  $\text{H}^+$
- The buffer cannot remove  $\text{H}^+$  ions from the body but it temporarily acts as a shock absorbent to reduce free  $\text{H}^+$  ions.

# Buffers in the Body

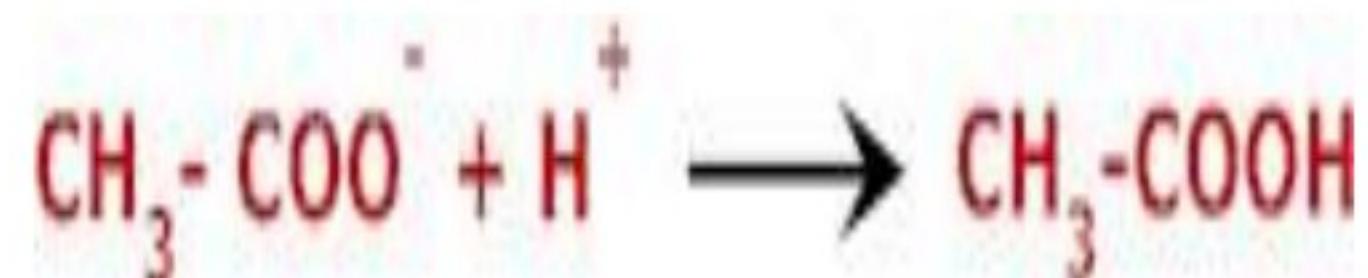
- Body fluids must be protected against change in pH. Because most enzymes are pH sensitive.
- During metabolism acids and bases are produced. In the long run, excess acids or base is eliminated via kidney and lungs. In the short run the body is protected against pH change by buffering systems. Acids produced by the body are carbonic acid, sulfuric acid, phosphoric acid, lactic acid, citric acid, ammonium ions Ketone bodies i. e. acetoacetic acid and  $\beta$ -hydroxybutyric acid.
- **Bicarbonate buffer is the major extracellular buffer and phosphate buffer is the major intracellular buffer in the body**, which protects the body against the pH change.

# Buffer Pair

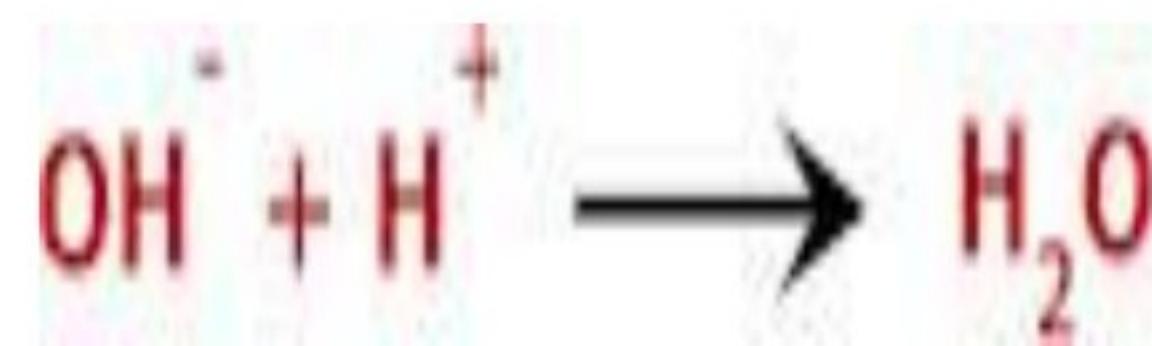
- Let us consider the buffer pair of acetic acid and sodium acetate.



- When an **acid** say HCl is added, the acetate ion of the buffer binds with  $\text{H}^+$  of HCl to form acetic acid, which is weakly ionized. Therefore the buffer resists the pH change due to acid.



- When a **base** say NaOH is added the  $\text{H}^+$  ions of the buffer acetic acid combines with  $\text{OH}^-$  ions to form water, which is weakly ionized. Thus the pH change due to base addition is also prevented.



# Henderson - Hasselbalch Equation

- A weak acid HA ionizes as follows :  $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$
- The equilibrium constant for this reaction is written as follows :  $K = [\text{H}^+][\text{A}^-] / [\text{HA}]$
- The value of the dissociation constant (K) indicates the tendency of the acid to lose its proton.  
Stronger acids have a greater tendency to dissociate and therefore have higher dissociation constant.

$[\text{HA}]$  = concentration of the un-dissociated acid,

$[\text{H}^+]$  = concentration of hydrogen ion and

$[\text{A}^-]$  = concentration of the conjugate base.

Cross multiplying:  $[\text{H}^+][\text{A}^-] = K [\text{HA}]$

$$[\text{H}^+] = K * ([\text{HA}] / [\text{A}^-])$$

- Taking -log of both sides  $-\log [\text{H}^+] = -\log K -\log ([\text{HA}] / [\text{A}^-])$
- Substitute pH and pK for  $-\log [\text{H}^+]$  and  $-\log K$  respectively. The  $-\log$  of the dissociation constant is defined as the pK.  $\text{pH} = \text{pK} - \log ([\text{HA}] / [\text{A}^-])$  (The stronger the acid, lower is its pK)
- Then to remove the -sign invert the last term  $\text{pH} = \text{pK} + \log ([\text{A}^-] / [\text{HA}])$

# Henderson - Hasselbalch equation

From

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

Rearrange

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

Take (-)Log of each

$$pH = -\log K + \log \frac{[A^-]}{[HA]}$$

$$pH = pK + \log \frac{[A^-]}{[HA]}$$

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

$\frac{[\text{A}^-]}{[\text{HA}]}$  ratio varies from  $\frac{1}{10} \Rightarrow \frac{10}{1}$

Above and below this range there is insufficient amount of conjugate acid or base to combine with the base or acid to prevent the change in pH.

## For weak acids



This equilibrium depends on concentrations of each component

If  $[\text{HA}] = [\text{A}^-]$  or 1/2 dissociated

Then

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = \log 1 = 0 \quad : \text{pH} = \text{pK}$$

- By definition the pK is the pH where  $[\text{HA}] = [\text{A}^-]$  : 50% dissociated
- The buffer effect can be seen in a titration curve.
- To a weak acid salt,  $\text{CH}_3\text{COO}^-$ , add HCl while monitoring pH vs. the number of equivalents of acid added.

# Factors Determining the Effectiveness of Buffer

- Two factors determine the effectiveness of buffer
  - Its **pK related to pH of the solution**
  - **Concentration**
- A buffer works best within 1 pH unit above or below its pK
- A buffer is more effective the more concentrated it is. Because the more concentrated solution contains more buffer molecules.
- A 1M solution of a given buffer has 1 million ( $10^6$ ) times more buffering molecules than 1  $\mu\text{m}$  ( $10^{-6}$ ) solution
- Greater the buffering capacity, the less the change of pH
- When the pH is equal to pK, the concentration of conjugate base is equal to concentration of un-dissociated acid.

**THANKS**