Chapter 17

Acid – Base Equilibria
&
Solubility Equilibria

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Buffer Solutions (Buffers)

Solutions that resist changes in pH when small amounts of acid or base are added

- Must contain a <u>weak</u> acid or base **<u>and</u>**
- The <u>conjugate</u> (salt) of the weak acid or base
- i.e. Contain a weak conjugate acid/base pair
- pH is controlled by equilibrium [K_a (or K_b)]

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

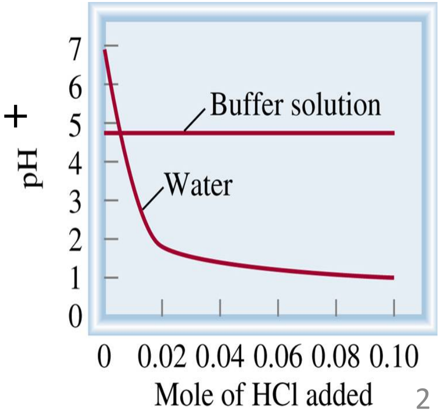
When small amounts of a strong acid or base are added:

- Acidic species in buffer neutralizes added OH^-

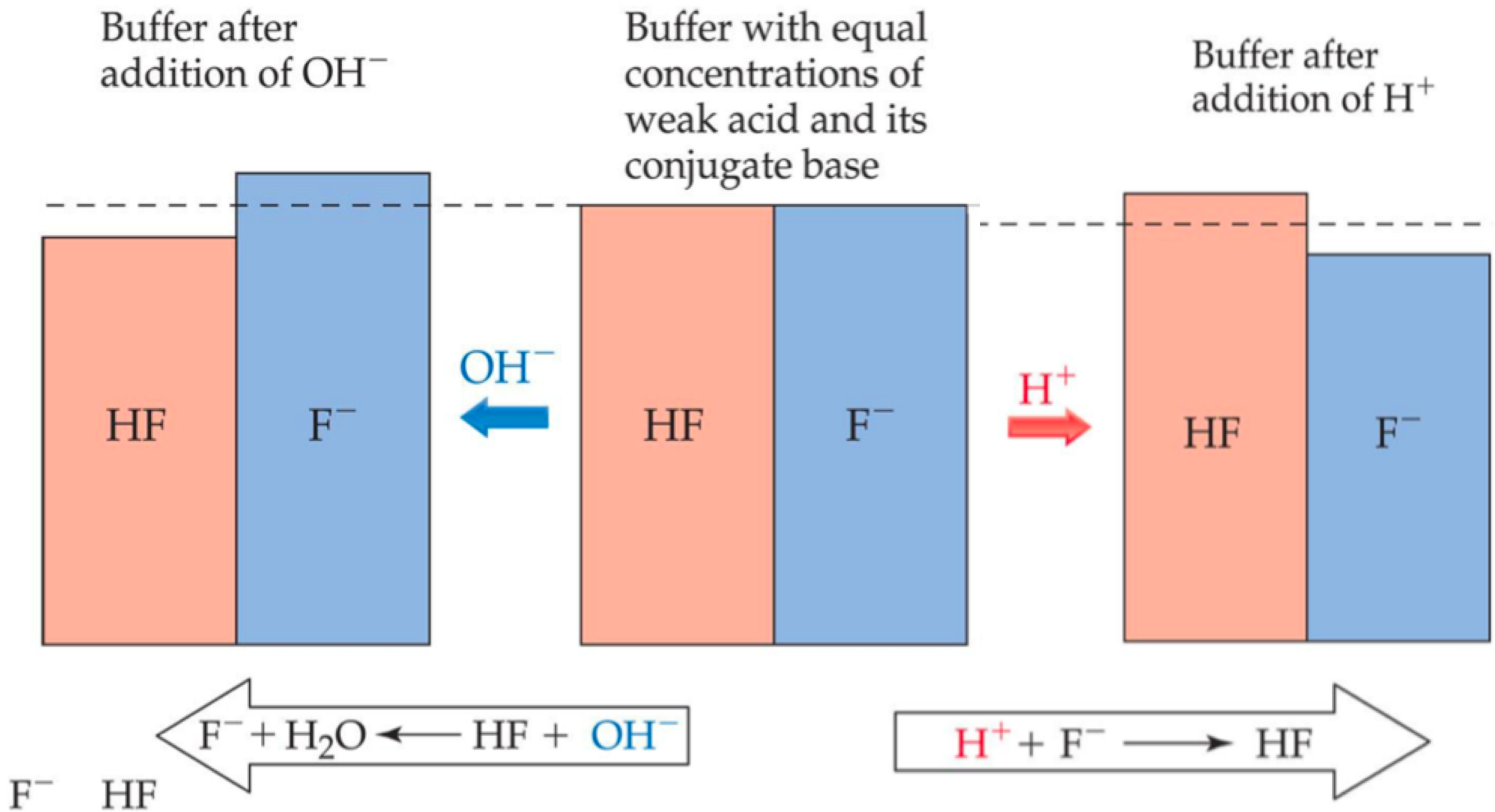
$$HA + OH^- \rightleftharpoons H_2O + A^-$$

- Basic species in buffer neutralizes added H^+

$$A^- + H_3O^+ \rightleftharpoons H_2O + HA$$



How Buffers Work – Le Châtelier's Principle



$$HF \rightleftharpoons H^+ + F^-$$

- Add OH^-, reduce H^+, shift equilibrium toward conj. Base
  - OH^- will react with H^+ to form water
- Add H^+, shift equilibrium toward undissociated acid

Henderson–Hasselbalch Equation

$$\boxed{\mathbf{pH = pK_a + \log \frac{[A^-]}{[HA]}}}$$

Comes from the equilibrium expression for: $HA \rightleftharpoons H^+ + A^-$

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

Take the –log of both sides:

$$\underbrace{-\log K_a}_{pK_a} = \underbrace{-\log [H^+]}_{pH} + -\log \frac{[A^-]_{\text{Conj. base}}}{[HA]_{\text{acid}}}$$

Therefore:

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

For bases:

$$pOH = pK_b + -\log \frac{[BH^+]}{[B]}$$

Rearrange to get Henderson-Hasselbalch

Using the Henderson-Hasselbalch Equation

1. A 1.00L buffer solution is prepared that contains 0.150M nitrous acid and 0.200M sodium nitrite. What is its pH?

$K_a = 7.2x10^{-4}$

Ice Table Method

pH = 3.27

Using the Henderson–Hasselbalch Equation

1. A 1.00L buffer solution is prepared that contains 0.150M nitrous acid and 0.200M sodium nitrite. What is its pH?

$K_a = 7.2x10^{-4}$

H-H equation method:

pH = 3.27

Using the Henderson–Hasselbalch Equation

2. How many grams of sodium lactate ($CH_3CH(OH)COONa$) should be added to 1.0L of a 0.150M lactic acid ($CH_3CH(OH)COOH$) to form a buffer solution with pH=4.00? K_a = $1.4x10^{-4}$; molar mass of sodium lactate = 112.1g/mol

A: 24g

Buffer Capacity

Buffer Capacity: **The amount of acid or base a buffer can neutralize before there is a significant change in pH.**

- Ratio of weak base to weak acid ($[A^-]/[HA]$) should be between 0.1 & 10.
- Most effective when $[A^-] = [HA]$ (i.e. ratio = 1)
  - Equal ability to neutralize acids & bases
- Buffer capacity depends on:
  - K_a of the acid
  - Concentration of buffer components
    - More concentrated = higher capacity

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

pH Range

pH Range: **The range of pH values over which a buffer system works effectively**

- Best to choose an acid with a pK_a close to the desired pH
- If $[A^-] = [HA]$, then $pH = pK_a$

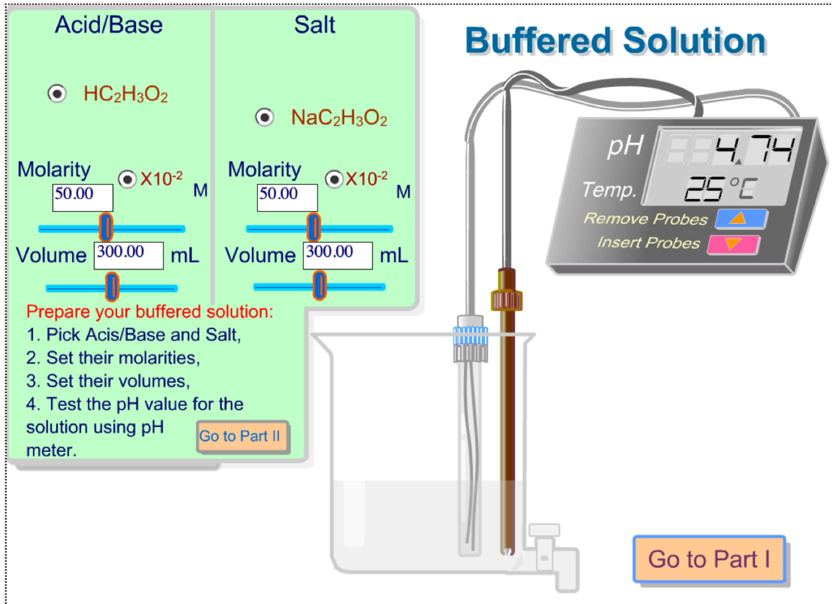
$$\boxed{\mathbf{pH = pK_a + \cancel{\log \frac{[A^-]}{[HA]}}}}$$

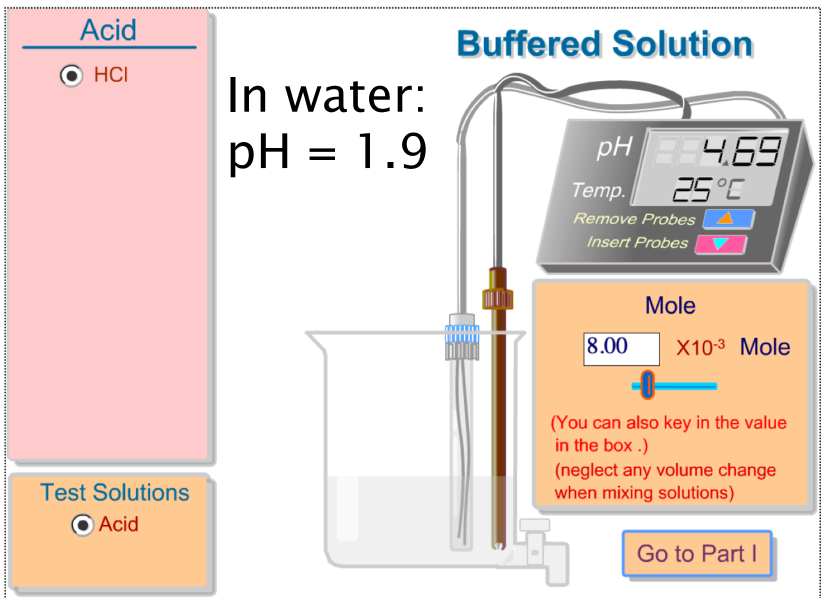
$\log(1) = 0$

- Buffer generally usable withing ± 1 pH unit of the pK_a

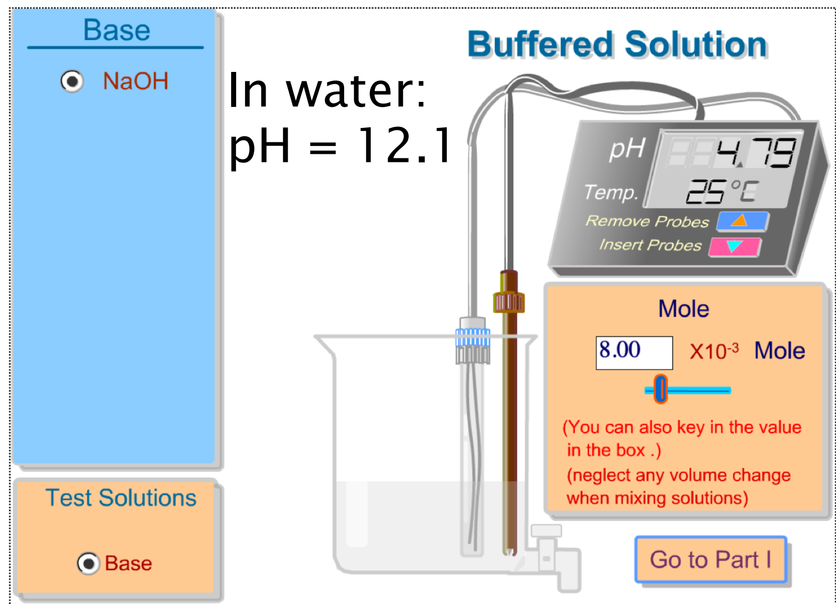
Criteria for Making a Buffer

1. **Choose a weak acid & conjugate base**
   - Must have the same anion!
     - ex. HNO_2 & $NaNO_2$; HF & LiF
2. **Select acid based on desired pH range**
   - $pK_a < 7$ buffer is acidic; $pK_a > 7$ buffer is basic
   - Buffers can usually be adjusted to ±1 desired pH
3. **Buffer salts (conjugate base) must be soluble & dissociate completely**
   - Most commonly sodium or potassium salts
   - NH_4^+ salts are acidic because NH_4^+ dissociates
4. **Concentrations of [HA] & [A$^-$] > 0.01M**
   - Must be able to neutralize sufficient acid/base
   - Can use ICE table to get an idea of what concentration is needed.





In water:
pH = 1.9



In water:
pH = 12.1

https://pages.uoregon.edu/tgreenbo/pHbuffer20.html

Buffer calculations

1. A 1.0 L buffer solution contains 0.150 M nitrous acid and 0.200 M sodium nitrite. K_a=7.2x10^{-4} (a) What is the pH of the buffer? (b) What is the pH after adding 1.00 g HBr?

A: (a) 3.27
(b) 3.21

Buffer calculations

2. A buffer is made by adding 0.600 mol CH_3COOH and 0.600 mol CH_3COONa to enough water to make 2.00L of solution. $K_a = 1.8x10^{-5}$.

(a) What is the pH of the buffer? A: 4.74

(b) Calculate the pH after 0.040 mol HCl is added. A: 4.69

(c) Calculate the pH after 0.040 mol NaOH is added. A: 4.80