# Section 19.1. Acid-Base Buffer Solutions

In everyday English, a buffer is something that lessens the impact of an external force.

\*\* An acid-base buffer is a solution that lessens the change in [H<sub>3</sub>O<sup>+</sup>] that would result when a strong acid or base is added \*\*

A buffer is a concentrated solution of a weak acid (or base), together with a salt containing the conjugate base (or acid).

*i.e.*, a weak acid and its conjugate base

<u>or</u> a weak base and its conjugate acid.

How does a Buffer work? The Common-Ion Effect

(example of Le Chatelier's Principle)

= the shift in an equilibrium caused by the addition (or removal) of one of the species participating in the equilibrium.

**Example:** addition of sodium acetate ( $CH_3COONa$  or NaAc) to acetic acid ( $CH_3COOH$  or HAc) solution

CH<sub>3</sub>COOH (aq) + H<sub>2</sub>O (l) acetic acid (HAc) acetate ion (Ac<sup>-</sup>) white add CH<sub>3</sub>COO<sup>-</sup> SHIFT <u>Net Effect</u>: [H<sub>3</sub>O<sup>+</sup>] decreases Also, [OH<sup>-</sup>] increases SHIFT Met Effect: [H<sub>3</sub>O<sup>+</sup>] decreases SHIFT Met Effect: [H<sub>3</sub>O<sup>+</sup>] decreases SHIFT SHI



**<u>Example</u>**: addition of  $NH_4CI$  to  $NH_3$  solution.

$$NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq)$$
  
if we add  $NH_4^+$ 



New type of problem to solve! - solutions with two things dissolved

**Example:** Calculate  $[H_3O^+]$  in a solution that is 0.10 M in HF and 0.20 M in NaF. Also calculate % ionization. **<u>Problem</u>**: Use HF (aq) = H<sup>+</sup> (aq) + F<sup>-</sup> (aq)? or F<sup>-</sup> (aq) + H<sub>2</sub>O (I) = HF (aq) + OH<sup>-</sup> (aq)? **Answer**: Since both include HF, F<sup>-</sup>, H<sup>+</sup>, OH<sup>-</sup> (the last two are related by  $[H^+][OH^-] = 1 \times 10^{-14}$ , we can use either equation !!  $HF(aq) = H^{+}(aq) + F^{-}(aq)$ [init]0.10 M00.20 M[change] -x+x+x[equil](0.10-x)x(0.20+x) $K_{a} = \frac{[H^{+}][F^{-}]}{[HF]} = 6.8 \times 10^{-4} = \frac{x(0.20 + x)}{(0.10 - x)} \approx \frac{0.20 \times 10^{-4}}{0.10}$  $\therefore$  x = (0.10) (6.8 × 10<sup>-4</sup>)/0.20 = 3.4 × 10<sup>-4</sup> M (x << 0.10)  $\therefore$  [H<sup>+</sup>] = [H<sub>3</sub>O<sup>+</sup>] = 3.4 × 10<sup>-4</sup> M Compare: in pure 0.1 M HF,  $[H_3O^+] = 8.5 \times 10^{-2} M$ in pure 0.2 M NaF,  $[H_3O^+] = 6.0 \times 10^{-9} M$ % ionization of HF =  $([H^+]/[HF])$  100% =  $(3.4 \times 10^{-4})$  100% = 0.34% **Compare:** For pure 0.1 M HF, % ionization is 8.5%

 $\therefore$  the presence of NaF in the solution has <u>decreased</u> the % ionization of HF (equilibrium shifted to the left)  $\therefore$  less [H<sub>3</sub>O<sup>+</sup>]  $\therefore$  less acidic.



Now, let's go back and see how a buffer works: It is a solution containing high concentrations of a weak acid (base) and its conjugate base (acid).

 $\begin{array}{ll} CH_{3}COOH(aq) \ = \ H^{+}(aq) \ + \ CH_{3}COO^{-}(aq) \\ acetic \ acid \ (HAc) & acetate \ ion \ (Ac^{-}) \end{array}$ 

**<u>If strong acid added</u>**:  $H^+ + Ac^- \rightarrow HA$  (K>>1 : assume rxn goes ~100%)

**If strong base added:**  $OH^- + HA \rightarrow H_2O + Ac^-$  (K>>1 : assume rxn goes ~100%)

Reactions go strongly to right  $\therefore$  [H<sup>+</sup>] and [OH<sup>-</sup>] in the solution change little. Similar logic for weak base (*e.g.*, NH<sub>3</sub>) and salt (*e.g.*, NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>).

\*\* <u>As long as not too much strong acid or base is added, it will be</u> "mopped-up" by the buffer and pH will change only slightly \*\*

Figure	19.2
Figure	19.3

change of pH on addition of strong acid or base.

3 change of [HA]/[A<sup>-</sup>] on addition of strong acid or base.



# Figures 19.1 and 19.2

### The effect of adding acid or base to an unbuffered solution.





#### The effect of adding acid or base to a **buffered** solution.



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# Figure 19.3 How a buffer works.





**Buffer Calculations:** Two types we must be able to handle:

- (A) Calculate the pH (or pOH,  $[H_3O^+]$ ,  $[OH^-]$ ) of a buffer solution
- (B) Calculate new pH (or pOH, ...) after something is added

#### Example: Sample Problem 19.1

(1) Calculate pH of a solution that is 0.50 M HAc and 0.50 M NaAc.  $K_a = 1.8 \times 10^{-5}$ .

	HAc (aq)	$\rightleftharpoons$	H⁺(aq)	+	Ac⁻(aq)
[init]	0.50 M		0		0.50 M
[change	] -×		+X		+X
[equil]	(0.50-x)		X		(0.50+x)
$K_a = \frac{x(a)}{a}$	$\frac{0.50+x}{0.50-x} \approx -\frac{1}{2}$	0.50x 0.50	= x = 1.8 x	10 <sup>-5</sup>	
∴ [H₃O	<sup>+</sup> ] = 1.8 × 10 <sup>-</sup>	<sup>5</sup> M ∴	pH = 4.74	1	



(2) What is the new pH after 0.020 mol of solid NaOH is dissolved in 1.0 L of the buffer solution?  $\begin{bmatrix} 0.020 \text{ mol} \\ 1.0 \text{ L} \end{bmatrix} = \begin{bmatrix} 0.020 \text{ mol} \\ 1.0 \text{ L} \end{bmatrix} = 0.020 \text{ mol}/\text{L} = 0.020 \text{ M}$ 

NaOH is a strong base : dissociates 100% : [OH-] = 0.020 M

What will happen when we add the NaOH? All the added OH<sup>-</sup> will react with HAc to give more Ac<sup>-</sup>. Keep track of changes with a table:

 $\therefore$  new [HAc] = 0.48 M , new [Ac<sup>-</sup>] = 0.52 M

Now calculate new pH

$$\begin{array}{rcl} & \text{HAc } (aq) & \Rightarrow & \text{H}^{+}(aq) & + & \text{Ac}^{-}(aq) \\ [\text{init]} & 0.48 \text{ M} & 0 & 0.52 \text{ M} \\ [\text{change]} & -x & +x & +x \\ [\text{equil]} & (0.48 - x) & x & (0.52 + x) \\ & K_{a} = & \frac{(0.52 + x)x}{0.48 - x} \approx & \frac{0.52x}{0.48} & = 1.8 \times 10^{-5} \\ & x = = 1.7 \times 10^{-5} \text{ M} & (\text{assumption okay}) \\ & \therefore & [\text{H}_{3}\text{O}^{+}] = 1.7 \times 10^{-5} \text{ M} & \therefore & \text{pH} = 4.77 \end{array}$$



(3) What is the new pH if 0.020 mol HCl had been added to (1) (instead of 0.020 mol NaOH)?

 $[HCI] = 0.020 \text{ M} \therefore [H_3O^+] = 0.020 \text{ M} (100\% \text{ dissociation})$ 

What will happen when we add the H<sup>+</sup> (=  $H_3O^+$ )? All of it will react with Ac<sup>-</sup> to give more HAc. Keep track of changes with a table:

 $Ac^{-}(aq) + H_{3}O^{+}(aq) \rightarrow HAc(aq) + H_{2}O(l)$ [init] 0.50 M 0.50 M [addition] 0.020 M [equil] 0.48 M 0.52 M 0 New [HAc] = 0.52 M New  $[Ac^{-}] = 0.48 \text{ M}$ Now calculate new pH  $HAc(aq) \rightleftharpoons H^{+}(aq) + Ac^{-}(aq)$ 0.52 M 0.48M [init] 0 change -x +x [equil] (0.52-x) x +X (0.48-x)  $K_a = \frac{x(0.48 - x)}{(0.52 - x)} \approx \frac{0.48x}{0.52} = 1.8 \times 10^{-5}$ ∴ x = (0.52)(1.8 × 10<sup>-5</sup>)/0.48 = 2.0 × 10<sup>-5</sup> M ∴  $[H_3O^+]$  = 2.0 × 10<sup>-5</sup> ∴ pH = 4.70

Again, the pH has changed only slightly, even though a significant

amount of strong acid was added. BUFFERS WORK!!



#### Henderson-Hasselbalch Equation

#### \*\* This allows us to calculate the pH without calculating [H<sup>+</sup>] first! \*\*

It can be shown for a solution of a weak acid HA that the pH, [HA] and [A<sup>-</sup>], and the pK<sub>a</sub> of the acid are related by  $pH = pK_a + log\left(\frac{[A^-]}{[HA]}\right)$ 

or, for any weak acid/conjugate base, or weak base/conjugate acid

$$pH = pK_a + log\left(\frac{[base]}{[acid]}\right)$$

$$\frac{\text{Let's apply H-H eqn. to our sample problem 19.1}}{\text{pK}_{a} = -\log (1.8 \times 10^{-5}) = 4.74}$$
(1) pH = pK\_{a} + log  $\frac{[\text{Ac}^{-}]}{[\text{HAc}]} = 4.74 + \log \left(\frac{0.50}{0.50}\right) \therefore \text{ pH} = 4.74$  (since log 1 = 0)  
(2) pH = 4.74 + log  $\left(\frac{0.52}{0.48}\right) = 4.77$   $\therefore \text{ pH} = 4.77$   
(3) pH = 4.74 + log  $\left(\frac{0.48}{0.52}\right) = 4.70$   $\therefore \text{ pH} = 4.70$ 

Two methods give same answers (within rounding errors on sig. figs.)



<u>Calculations also involving volume changes</u>: (extra complication to deal with) <u>Example</u>: A buffer is prepared from 60.0 mL of 0.100 M NH<sub>3</sub> and 40.0 mL of 0.100 M NH<sub>4</sub>Cl. What is the pH of the buffer solution?  $K_b = 1.8 \times 10^{-5}$  for NH<sub>3</sub>.

<u>Answer</u>: The buffer involves the  $NH_3/NH_4^+$  conjugate acid/base pair.  $NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq)$ 

<u>Conc's</u>: Since two solutions are mixed, both have been diluted.

<u>Use this</u>:  $V_i M_i = V_f M_f$   $V_f = 60.0 \text{ mL} + 40.0 \text{ mL} = 100.0 \text{ mL}$  $[NH_3]_f = V_i M_i / V_f = (60.0 \text{ mL})(0.100 \text{ M}) / 100.0 \text{ mL} = 0.0600 \text{ M}$  $[NH_4^+]_f = V_iM_i/V_f = (40.0 \text{ mL})(0.100 \text{ M})/100.0 \text{ mL} = 0.0400 \text{ M}$ Now, we can calculate pH:  $NH_{3}(aq) + H_{2}O(l) = NH_{4}^{+}(aq) + OH^{-}(aq)$ 0.0600 0.0400 [init] 0 [change] -x +X +X [equil] (0.0600-x) (0.0400+x) x  $K_{\rm b} = 1.8 \times 10^{-5} = \frac{\times (0.0400 + x)}{0.0400 \times 10^{-5}} \approx 0.0400 \times ... \times = = 2.7 \times 10^{-5} \,\text{M}$ (0.0600 - x) 0.0600 ∴ pOH =  $-\log (2.7 \times 10^{-5}) = 4.57$  ∴ | pH = 9.43 If we now add strong acid or base, we would again have to calculate new total

If we now add strong acid or base, we would again have to calculate new total volume and new [NH<sub>3</sub>] and [NH<sub>4</sub><sup>+</sup>] and [acid or base] to calculate new pH. 19-11

# Buffer Capacity and Buffer Range

(A) Buffer Capacity is how much added acid or base a buffer solution can "mop up" before it can no longer resist changes in the pH.

# \*\* The more concentrated the components of the buffer, the greater the buffer capacity \*\*.

Thus, a buffer containing 0.10 M NH<sub>3</sub>/0.10 M NH<sub>4</sub><sup>+</sup> is good, but a buffer containing 1.0 M NH<sub>3</sub>/1.0 M NH<sub>4</sub><sup>+</sup> is much better.

**Note:** Since  $[NH_3]/[NH_4^+]$  is 1 in both cases, they both have pH = 4.74, but very different buffer capacities.

Also, the more similar the conc's of the two components, the higher is the buffer capacity. The greater the difference, the greater will be the pH change when strong acid or base is added.

\*\* buffer capacity highest when [HA] = [A<sup>-</sup>] \*\* From the H-H eqn:  $pH = pK_a + \log \frac{[A^-]}{[HA]}$  ... when  $[A^-] = [HA]$ ,  $\log \frac{[A^-]}{[HA]} \log 1 = 0$  $\therefore pH = pK_a$  gives the highest buffer capacity

**\*\*** Summarizing: Buffer capacity is highest when:

- (1) [HA] and  $[A^-]$  are large
- (2)  $[HA] = [A^-]$
- (3) The pH is equal to (or very near) the  $pK_a$  of the HA used.\*\*



# Figure 19.4 The relation between buffer capacity and pH change.



This graph shows the final pH values for four different buffer solutions after the addition of strong base.



**Example:** Which is the best acid to use to make a buffer solution with a pH = 2.0. Acetic acid ( $pK_a = 4.74$ ); chlorous acid ( $pK_a = 1.95$ ) or formic acid ( $pK_a = 3.74$ ).

To ensure high capacity, we need [HA]  $\approx$  [A<sup>-</sup>]. It is possible to get this <u>and</u> have a pH = 2.0 only if we use chlorous acid since its pK<sub>a</sub> is close to the target pH we need.

 $\therefore$  the answer is **chlorous acid (HClO**<sub>2</sub>).

(B) Buffer Range is the pH range over which the buffer acts effectively. The further the  $[A^-]/[HA]$  ratio from 1, the less effective is the buffer. Useful range is when pH of solution =  $pK_a \pm 1$ , but the closer to the acid's  $pK_a$ , the better.

Section 19.2. ACID/BASE TITRATION CURVES \*\*(NOT COVERING IN CLASS - GO OVER YOURSELVES AND IN DISCUSSION PERIODS)\*\*



Sample Problem 19.2 Using Molecular Scenes to Examine Buffers Consider four HA/A<sup>-</sup> buffers.

(HA is blue and green, A<sup>-</sup> is green (other ions and water are not shown.)



- (a) Which buffer has the highest pH? Highest [A-]:[HA] ∴ buffer 4
- (b) Which buffer has the greatest capacity?
   Highest concs and [A<sup>-</sup>] = [HA] ∴ buffer 3

Should we add a small amount of strong acid or strong base to

(c) Should we add a small amount of strong acid or strong convert 1 to 2 (assuming no volume changes)? Strong acid

Remember: 
$$pH = pK_{\alpha} + \log \frac{[A^{-}]}{[HA]}$$

log (>1) is positive log (1) is zero log (<1) is negative



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