#### **Chapter 18: Aqueous Ionic Equilibria I**

Buffers

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#### Introduction

- Aqueous solutions are extremely important: Acids and bases are aqueous solutions
- Equilibria influence aqueous solutions:

We can describe the behavior of an acid or base in terms of equilibrium

- How does equilibrium affect mixtures of acids and bases?
- How does equilibrium affect the solubility of compounds in water?



#### **Buffer solutions**



- The pH of blood must be maintained between about 7.3 and 7.5 to avoid death
- Aqueous equilibria in the blood control pH
- A buffer is a substance that resists changes in pH
- A buffer reacts with added acid or base with little change in overall pH
- In blood, the major components of the buffer consist of  $H_2CO_3$  and  $HCO_3^-$



<u>Conjugates!</u>

#### **Buffer solutions**

- Buffers contain significant quantities of an **acid and its conjugate base** (or a **base and its conjugate acid**)
  - Carbonic acid  $(H_2CO_3)$  + bicarbonate  $(HCO_3^{-})$
  - Ammonia (NH<sub>3</sub>) + ammonium ions (NH<sub>4</sub><sup>+</sup>)
- Consider an acetic acid (HCH<sub>3</sub>CO<sub>2</sub>) and (its conjugate base) acetate (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>) buffer:

Added **base** is neutralized by the **acid**  $HCH_3CO_2$ Added **acid** is neutralized by the **conjugate base**  $CH_3CO_2^-$ 

### No change in pH!











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#### Identifying buffer solutions

Which solution is a buffer?

- $\bullet$  0.100 M HNO\_2 and 0.100 M HCl
- 0.100 M HNO $_3$  and 0.100 M NaNO $_3$
- $\bullet$  0.100 M HNO\_2 and 0.100 M NaCl
- $\bullet$  0.100 M HNO\_2 and 0.100 M NaNO\_2

(HNO<sub>2</sub> is a weak acid with  $NO_2^-$  as conjugate base)





#### The pK<sub>a</sub> scale



One more common "p scale" used in chemistry uses  $K_a$  values to indicate the strength of an acid:

 $pK_a = -log(K_a)$ 

Remember, the larger the value of  $K_a$ , the stronger the acid.

**Example.** What is the  $pK_a$  of formic acid if  $K_a = 1.8 \times 10^{-4}$ ?

$$pK_a = -\log(1.8 \times 10^{-4}) = 3.74$$

The smaller the  $pK_a$ , the stronger the acid.  $pK_b$  can also be defined in a similar way (for bases).



#### How buffers work?



Consider acetic acid / acetate buffer.

1. Added base is neutralized by the acid HCH<sub>3</sub>CO<sub>2</sub>:

 $OH^{-}(aq) + HCH_{3}CO_{2}(aq) \rightleftharpoons CH_{3}CO_{2}^{-}(aq) + H_{2}O(l)$ 

Addition of OH= (base) shifts the equilibrium right:

- As long as the amount of  $OH^{-}$  added is small compared with the amount of  $HCH_{3}CO_{2}$ , it is almost completely neutralized.

-  $CH_3CO_2^{-1}$  is weakly basic, so pH would rise slightly.



#### How buffers work?



2. Added acid is neutralized by the conjugate base  $CH_3CO_2^-$ : H<sup>+</sup>(aq) +  $CH_3CO_2^-$ (aq)  $\rightleftharpoons$  HCH<sub>3</sub>CO<sub>2</sub>(aq)

#### Addition of H<sup>±</sup> shifts the equilibrium right:

- As long as the amount of  $H^+$  added is small compared with the amount of  $CH_3CO_2^-$ , it is almost completely neutralized.

-  $HCH_3CO_2$  is weakly acidic, so pH would drop slightly.

- Acetic acid by itself is **not a good buffer** because the amount of  $CH_3CO_2^{-1}$  available is very small!





#### How buffers work?





Addition of acid:  $HCI(aq) + NaCH_{3}CO_{2}(aq) \rightleftharpoons$  $HCH_{3}CO_{2}(aq) + NaCI(aq)$ 

Addition of base: NaOH(aq) +  $HCH_3CO_2(aq)$  $\Rightarrow$  NaCH\_3CO\_2(aq) + H\_2O(I)



#### **Calculating buffer pH**



- At first sight, calculating the pH of a mixture of acid and base might seem difficult.
- But the **common ion effect** simplifies the problem:

 $HCH_{3}CO_{2}(aq) \rightleftharpoons H^{+}(aq) + CH_{3}CO_{2}(aq)$ 

- Adding extra conjugate base (the common ion) suppresses ionization of the acid (Le Châtelier)
- The initial concentrations of the acid and added conjugate base don't change significantly



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#### Calculate the pH of a buffer – ICE table approach

**Example.** What is pH of a solution that is 0.100 M  $HC_2H_3O_2$  and 0.100 M  $NaC_2H_3O_2$  ( $K_a = 1.8 \times 10^{-5}$ )?

	CH₃COOH(aq)	H <sub>2</sub> O(I)	⇒	H₃O+(aq)	CH₃COO⁻(aq)
1	0.100 M	-		~0 M	0.100 M
<u>C</u>	-X	-		+x	+x
<u>E</u>	0.100 - <i>x</i>	-		X	0.100 + <i>x</i>

$$K_a = \frac{\left[\mathrm{H}_3\mathrm{O}^+\right] \left[\mathrm{CH}_3\mathrm{COO}^-\right]}{\left[\mathrm{CH}_3\mathrm{COOH}\right]} = \frac{x(0.100+x)}{0.100-x} \approx x$$

and solve for *x*.  $pH = -log([H_3O^+]) = 4.74$ .



#### **Henderson-Hasselbalch Equation**



A simplified way to solve for pH from **initial concentrations**:

$$HA(aq) + H_2O(\ell) \Longrightarrow H_3O^+(aq) + A^-(aq)$$
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

- $[H_3O^+]$  is proportional to the ratio of  $[HA] / [A^-]$
- Take the -log of both sides to get the Henderson-Hasselbalch (H-H) equation:

Initial concentrations

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



#### **Henderson-Hasselbalch Equation**



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

- In order to use the initial concentrations above, we assume that the acid dissociation is small (i.e., x is small in the ICE table approach).
- For this to hold K<sub>a</sub> must be small (weak acid) and comparable amounts of HA and A<sup>-</sup> must be present to minimize dissociation.
  Notes:
- log(1) = 0, so if [base] = [acid], buffer pH = pK<sub>a</sub>
- The base and acid are in the same solution, so you can use moles instead of molarity above (the volumes cancel)
- H-H equation works ONLY for buffer solutions!



#### **Henderson-Hasselbalch Equation**



**Example.** Calculate the pH of a solution of 0.34 M lactic acid  $(K_a = 1.4 \times 10^{-4})$  and 0.22 M potassium lactate.

We <u>must</u> recognize this as a buffer solution with [HA] = 0.34M and  $[A^{-}] = 0.22$  M. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[A^-]_{initial}}{[HA]_{initial}}\right)$$
  
How do we find this?  
 $pK_a = -\log K_a$   
 $pH = pK_a + \log\left(\frac{0.22}{0.34}\right) = 3.85 - 0.19 = 3.66$ 



#### Exercise



# Calculate the pH of a solution that is 0.195 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and 0.125 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> ( $K_a = 1.8 \times 10^{-5}$ ).

[This can be solved using either ICE chart or the Henderson-Hasselbalch equation but need to confirm that it is buffer solution]



#### Calculating changes in buffer pH



- While buffers resist changes in pH upon addition of strong acid or base, the pH does still change slightly.
- We find out how much by breaking the pH calculation into two parts:
  - 1. Stoichiometry calculation

 Use stoichiometry to find out how much conjugate base is neutralized by addition of strong acid or

 Use stoichiometry to find out how much acid is neutralized by addition of strong base

2. Equilibrium calculation

Use Henderson-Hasselbalch calculation (or ICE table)



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#### Addition of acid or base to a buffer solution

- If you add acid to a buffer, the pH must decrease slightly.
- If you add base to a buffer, the pH must increase slightly.
- Adding strong acid removes some of the conjugate base.
- Adding strong base removes some of the weak acid.
- After addition, a new equilibrium is established.





**Example 1.** Calculate the pH of a solution of 1.00 L of 0.34 M lactic acid ( $K_a = 1.4 \times 10^{-4}$ ) and 0.22 M potassium lactate after addition of 0.05 L of 1.0 M HCl.

#### **1. Stoichiometry calculation**

Addition of strong acid uses up some of the conjugate base (A<sup>-</sup>) and makes more lactic acid (HA):

 $H^{+}(aq) + A^{-}(aq) \rightleftharpoons HA(aq)$ 

Remember HA is a weak acid so equilibrium lies mostly on the right.





It's easiest to work in terms of moles rather than concentration as the total volume may change.

Moles of  $A^{-} = 1.00 L \times 0.22 M = 0.22$  moles Moles of HA = 1.00 L x 0.34 M = 0.34 moles Moles of H<sup>+</sup> added = 0.05 L x 1.00 M = 0.05 moles

	H⁺(aq)	+ $A^{-}(aq) \rightarrow$	HA(aq)
Initial	0.00 mol	0.22 mol	0.34 mol
Addition	<u>0.05 mol</u>	Decreases	Increases
Final	0.00 mol	0.17 mol	0.39 mol







How do you know whether the [HA] concentration increases or decreases?

- The addition of strong acid increases [HA]; equilibrium shifts right.
- The addition of strong base increases [A-]; equilibrium shifts left.



#### **2. Equilibrium calculation**

We'll convert the moles back into concentration:

$$A^{-}$$
] = 0.17 mols / 1.05 L = 0.16 M

and use the Henderson-Hasselbalch equation:

$$pH = pK_{a} + \log\left(\frac{[A^{-}]_{initial}}{[HA]_{initial}}\right)$$
  
But use ICE table  
to check validity (x)...  
$$pH = 3.85 + \log\left(\frac{0.16}{0.37}\right) = 3.49$$





**Example 2.** Calculate the pH of a solution of 1.00 L of 0.34 M lactic acid ( $K_a = 1.4 \times 10^{-4}$ ) and 0.22 M potassium lactate after addition of 0.05 L of 1.0 M <u>NaOH</u>.

#### 1. Stoichiometry calculation

Addition of strong base uses up some of the acid (HA) and makes more lactate  $(A^{-})$ :

$$OH^{-}(aq) + HA(aq) \rightleftharpoons A^{-}(aq) + H_{2}O(l)$$

Addition of OH<sup>-</sup> pushes the equilibrium to the right.



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#### Addition of acid or base to a buffer solution

It's easiest to work in terms of moles rather than concentrations:

Moles of  $A^{-} = 1.00 L \times 0.22 M = 0.22$  moles Moles of HA = 1.00 L x 0.34 M = 0.34 moles Moles of OH<sup>-</sup> added = 0.05 L x 1.00 M = 0.05 moles

	OH <sup>-</sup> (aq) -	HA(aq) →	$A^{-}(aq)$
Initial	0.00 mol	0.34 mol	0.22 mol
Addition	<u>0.05 mol</u>	Decreases	Increases
Final	0.00 mol	0.29 mol	0.27 mol





2. Equilibrium calculation

We'll convert the moles back into concentration:

$$[HA] = 0.29 \text{ mols} / 1.05 \text{ L} = 0.28 \text{ M}$$
  
 $[A^{-}] = 0.27 \text{ mols} / 1.05 \text{ L} = 0.26 \text{ M}$ 

and use the Henderson-Hasselbalch equation:

$$pH = pK_a + log\left(\frac{[A^-]_{initial}}{[HA]_{initial}}\right)$$
  
But use ICE table  
to check validity (x)...  
$$pH = 3.85 + log\left(\frac{0.26}{0.28}\right) = 3.82$$





**Example 3.** Consider 1.0 L of buffer solution made from generic weak acid HA ( $pK_a = 4.82$ ;  $K_a = 1.5 \times 10^{-5}$ ) and its conjugate A<sup>-</sup>.

The initial concentrations are  $[HA] = [A^{-}] = 0.100$  M. What is the initial pH and the pH after adding 0.025 mol of a strong acid? Assume that volume remains constant (not usually the case in practice!).



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#### Addition of acid or base to a buffer solution

1. The initial pH of the buffer solution can be calculated by using the H-H equation:

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

$$pH = pK_a + \log\left(\frac{0.100M}{0.100M}\right) = pK_a + 0 = 4.82$$





2. Add 0.025 moles of strong acid. It will react completely with the conjugate base A<sup>-</sup>. Follow the stoichiometry!

	A⁻(aq)	H+(aq)	$\rightarrow$	HA(aq)	H <sub>2</sub> O(I)
<u>Before</u> addition	0.100 moles	0 moles		0.100 moles	
<u>Addition</u>	0 moles	0.025 moles		0 moles	
<u>After</u> addition	0.075 moles	0 moles		0.125 moles	





3. Establish new equilibrium (ICE table):

	HA(aq)	H <sub>2</sub> O(I)	÷	H₃O+(aq)	A⁻(aq)
<u> </u>	0.125 M	_		~0 M	0.075 M
<u>C</u>	-X	_		+ <i>x</i>	+x
<u>E</u>	0.125 - <i>x</i>	_		X	0.075 + <i>x</i>

$$K_a = 1.5 \times 10^{-5} = \frac{x(0.075 + x)}{0.125 - x} \approx \frac{0.075x}{0.125}$$
$$x = [H_3O^+] = K_a \left(\frac{0.125}{0.075}\right) = 2.5 \times 10^{-5} M \qquad pH = 4.60$$





Or use the H-H equation (avoids ICE table):

	HA(aq)	H <sub>2</sub> O(I)	4	H₃O+(aq)	A-(aq)
Ī	(0.125 M)	-		~0 M	0.075 M
<u>C</u>	-X	_		+ <i>x</i>	+X
<u>E</u>	0.125 - <i>x</i>	-		X	0.075 + <i>x</i>

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{0.075 + x}{0.125 - x}\right) \approx pK_a + \log\left(\frac{0.075}{0.125}\right)$$

pH = 4.60 (same answer)



#### **Does the answer make sense?**

Sanity check: We had a buffer and we added acid to it:

- Expect pH to drop slightly
- Here pH goes from 4.82 to 4.60 OK!

<u>Math:</u> log of a number less than one must be negative, so pH <  $pK_a$  when you have more base than acid.

<u>Remember:</u> Volume changes can be significant whenever a large volume of acid or base is added to a buffer.





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#### Adding base to a buffer solution?

**Exercise.** What if we added 0.025 moles of strong base to our original buffer?

- It will react with the weak acid, producing more of the conjugate base (HA concentration decreases)
- Establish new equilibrium (just like shown before)
- Expectation: pH will increase slightly
- To check your work: pH = 5.04



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#### **Action of a Buffer**





#### Buffers from a weak base and conjugate acid

The Henderson-Hasselbalch equation still applies!

**Example.** Buffer from 0.05 M NH<sub>3</sub> and 0.04 M NH<sub>4</sub>Cl For NH<sub>3</sub>:  $pK_b = 4.75$  ( $pK_a$  for NH<sub>4</sub><sup>+</sup> = 14.00 - 4.75 = 9.25)

$$pH = pK_a + log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = 9.25 + \log\left(\frac{0.05\ M}{0.04\ M}\right)$$

pH = 9.35

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#### **Buffer effectiveness**

Changes in buffer pH upon addition of a strong acid or base are smallest when:

- 1. The concentrations of HA and A<sup>-</sup> are equal
  - The buffer has equal reserves of both acid and base to neutralize additions
  - HA and A<sup>-</sup> concentrations should be within a factor of 10
  - Buffers work best when the  $pH = pK_a$  of the acid
- 2. The concentrations of HA and A<sup>-</sup> are large:
  - The concentrations of HA and A<sup>-</sup> don't change much upon additions of strong acid and base







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#### **Buffer effectiveness**

HA and A<sup>-</sup> concentrations should be within a factor of 10 for a reasonably good buffer:

$$pH = pK_{a} + \log\left(\frac{[A^{-}]}{[HA]}\right) \qquad \text{How does pH vary if} \\ we change ratio? \\ \text{We change ratio?} \\ pH = pK_{a} + \log\left(\frac{[10]}{[1]}\right) \qquad (2) \qquad pH = pK_{a} + \log\left(\frac{[1]}{[10]}\right) \\ pH = pK_{a} + 1 \qquad pH = pK_{a} - 1 \\ \text{How does pH vary if} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{How does pH vary if} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{How does pH vary if} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{We change ratio?} \\ \text{How does pH vary if} \\ \text{We change ratio?} \\ \text{We change ratio.} \\ \text{We change ratio.} \\ \text{We change ratio.} \\ \text{We change ra$$

The **buffer range** (the range of pH over which the buffer is effective) is  $pK_a \pm 1$ .



#### **Buffer effectiveness**



**Example.** Which of the two would be a better buffer: 0.1 M HA with 0.1 M A<sup>-</sup> or 0.001 M HA with 0.001 M A<sup>-</sup>.

The first buffer solution would be better simply because it has higher concentrations of HA and A<sup>-</sup> that can neutralize more acid or base added to the system.



#### **Buffer capacity**

- The **buffer capacity** is the **amount of strong acid or base that can be added to the buffer before it is destroyed.** Destroyed means that either the acid or conjugate base is completely used up.
- Buffer capacity increases as [HA] and [A-] increase:
  - A 0.5 M HA + 0.5 M A<sup>-</sup> buffer has a higher buffer capacity than a 0.1 M HA + 0.1 M A<sup>-</sup> buffer
  - A 0.5 M HA + 0.5 M A<sup>-</sup> buffer has a higher buffer capacity than a 0.5 M HA + 0.1 M A<sup>-</sup> buffer





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#### **Buffer capacity**

**Example.** A buffer is comprised of 0.10 mol HCH<sub>3</sub>CO<sub>2</sub> and 0.05 mol NaCH<sub>3</sub>CO<sub>2</sub>. Which of the following additions will destroy the buffer?

0.05 mol of NaCH<sub>3</sub>CO<sub>2</sub>?

**No** - this will simply increase [A<sup>-</sup>].

- 0.05 mol of NaOH?
  No this will use up half of the acid but leave half remaining.
- 0.05 mol of HBr?

**Yes** - this will use up all of the conjugate base leaving only the weak acid (not a buffer anymore).

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#### Making a buffer solution

Make a weak acid solution with a salt of the conjugate base, e.g.:

 $0.100~M~HNO_2$  and  $0.100~M~NaNO_2$ 

<u>Or:</u> Start with a weak acid and add enough strong base to create the conjugate base in solution:

Add 100 mL of 0.1 M NaOH to 100 mL of 0.2 M HNO $_2$ 

<u>Or:</u> Start with a weak base and add enough strong acid to create the conjugate acid in solution:

Add 100 mL of 0.1 M HCl to 100 mL of 0.2 M  $NH_3$ 







#### Making a buffer solution



**Example (Weak acid & strong base)**. Add 100 mL of 0.1 M NaOH to 100 mL of 0.2 M HNO<sub>2</sub>.

Start:  $(0.100 \text{ L})(0.2 \text{ mol/L}) = 0.02 \text{ mol HNO}_2$ Add:  $(0.100 \text{ L})(0.1 \text{ mol/L}) = 0.01 \text{ mol OH}^-$  added

The neutralization reaction goes to completion:

 $HNO_2(aq) + OH^-(aq) \longrightarrow NO_2^-(aq) + H_2O(\ell)$ 

because NaOH is a strong base.



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#### **Tracking the number of moles**

	HNO₂(aq)	OH <sup>-</sup> (aq)	$\rightarrow$	NO2 <sup>-</sup> (aq)	H <sub>2</sub> O(I)
<u>Before</u> addition	0.02 moles	0		0	
<u>Addition</u>	0	0.01 moles		0	
<u>After</u> addition	0.01 moles	0		0.01 moles	

End up with 0.01 mol of HNO<sub>2</sub> and 0.01 mol NO<sub>2</sub><sup>-</sup> in a total volume of 200 mL. Therefore:  $[HNO_2] = [NO_2^{-1}] = 0.05$  M (*equal*). **A buffer!** 



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#### Making a buffer with a specific pH

Which acid and its conjugate base (as a sodium salt) would you choose to create a buffer with pH = 7.35?

1)  $HCIO_2 (pK_a = 1.95)$ 2)  $HNO_2 (pK_a = 3.34)$ 3)  $HCOOH (pK_a = 3.74)$ 4)  $HCIO (pK_a = 7.54)$  (because  $pK_a \sim pH$ )

What would be the ideal molar ratio of acid to salt? 1:1 for maximum buffer capacity but adjust for required pH.