

UWO **CHEM 1302**

Winter 2025, Chapter 10 Notes



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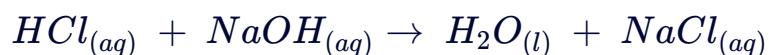
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10. Buffer Solutions

10.1 Acid + Base Reactions

10.1.1

Strong Base and Strong Acid Reactions



Case #1: Strong Acid is in Excess

(moles)	$HCl_{(aq)}$	$+ NaOH_{(aq)}$	$\rightarrow H_2O_{(l)}$	$+ NaCl_{(aq)}$
I	5	2	/	0
C	-2	-2	/	2
E	3	0	/	2

- We are left with moles of strong acid (HCl here) and moles of a neutral salt (NaCl here)
- To determine the pH of the resulting solution, take the moles of HCl we are left with and use it to find moles of H+, then we need to calculate [H+]
- $n=cv$ so $c=n/v=$ moles of H+/total volume of solution
- Then use $pH=-\log[H^+]$!

The resulting solution is strongly acidic!

Case #2: Strong Base is in Excess

(moles)	$HCl_{(aq)}$	$+ NaOH_{(aq)}$	$\rightarrow H_2O_{(l)}$	$+ NaCl_{(aq)}$
I	2	5	/	0
C	-2	-2	/	2
E	0	3	/	2

- We are left with moles of strong base (NaOH here) and moles of a neutral salt (NaCl here)
- To determine the pH of the resulting solution, take the moles of NaOH we are left with and use it to find the moles of OH-, then we need to calculate [OH-]
- $n=cv$ so $c=\text{moles of OH-}/\text{total volume of solution}$
- Calculate pOH using $pOH=-\log[\text{OH-}]$, and finally calculate pH using $pH+pOH=14$

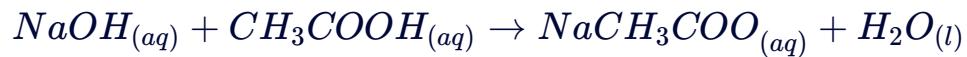
The resulting solution is strongly basic!

Case #3: Reacting the Same Amount of Moles of Strong Acid and Base

(moles)	$HCl_{(aq)}$	$+ NaOH_{(aq)}$	$\rightarrow H_2O_{(l)}$	$+ NaCl_{(aq)}$
I	5	5	/	0
C	-5	-5	/	5
E	0	0	/	5

- We are left with no moles of strong acid or strong base. **Only the neutral salt is left**
- This means the **pH=7 (neutral solution)**

Strong Base + Weak Acid Reactions



Case #1: Strong Base is in Excess

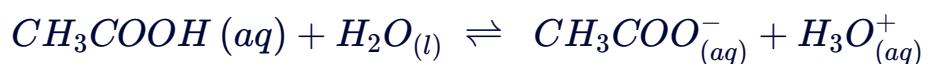
(moles)	$NaOH_{(aq)} + CH_3COOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$				
I	6	2	0	/	
C	-2	-2	2	/	
E	4	0	2	/	

- We are left with strong base and a weakly basic salt
- The resulting solution is strongly basic
- To determine the pH use the moles of strong base to find the moles of OH-, then using $n=cv$, solve for the concentration of OH-
- $[OH^-] = \text{moles of OH-} / \text{total volume of solution}$
- Calculate pOH using $pOH = -\log[OH^-]$, then calculate pH using $pH + pOH = 14$

Case #2: Weak Acid is in Excess

(moles)	$NaOH_{(aq)} + CH_3COOH_{(aq)} \rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$				
I	2	6	0	/	
C	-2	-2	2	/	
E	0	4	2	/	

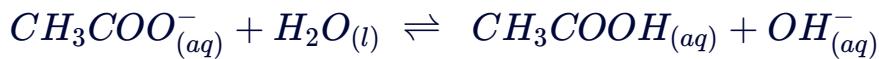
- The resulting solution has weak acid and a weakly basic salt
- Note:** We have a **conjugate acid** (CH_3COOH) **and its conjugate base** (CH_3COO^-)! These are the requirements for a buffer so we have a **buffer solution!** We will look at buffers soon :)



Case #3: React the Same Amount of Moles of Strong Base and Weak Acid

(moles)	$NaOH_{(aq)}$	$+ CH_3COOH_{(aq)}$	$\rightarrow NaCH_3COO_{(aq)} + H_2O_{(l)}$	
I	6	6	0	/
C	-6	-6	6	/
E	0	0	6	/

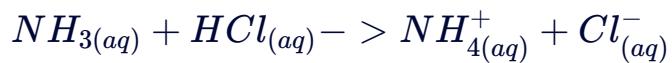
- We are only left with a weakly basic salt so the **solution is weakly basic**.
- To calculate pH of the resulting solution, we would need to consider the weak base:



- After using an ICE table and finding the number of moles of OH- we end up with, we can calculate [OH-] using $c=n/v=$ moles of OH-/total volume of solution
- Then calculate pOH, then finally pH

10.1.3

Weak Base + Strong Acid Reactions



Case #1: Strong Acid is in Excess

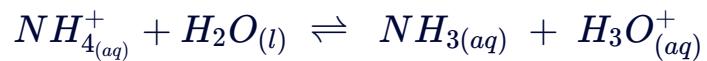
(moles)	$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_{4(aq)}^+ + Cl_{(aq)}^-$				
I	2	5	0	/	
C	-2	-2	2	/	
E	0	3	2	/	

- We are left with a strong acid and a weakly acidic salt
- The resulting solution is strongly acidic
- Determine the pH using moles of strong acid, find the [H+], find the pH

Case #2: Weak Base is in Excess

(moles)	$NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$			
I	5	2	0	/
C	-2	-2	2	/
E	3	0	2	/

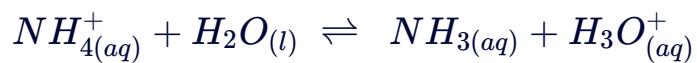
- We are left with a weak base and a weakly acidic salt
- Note: We have a **weak base** (NH_3) and its **conjugate acid** (NH_4^+) which are needed to form a **buffer!**



Case #3: Reacting the Same Amount of Moles of Strong Acid and Weak Base

(moles)	$NH_3(aq) + HCl_{(aq)} \rightarrow NH_4^+_{(aq)} + Cl^-_{(aq)}$				
I	2	2	0	/	
C	-2	-2	2	/	
E	0	0	2	/	

- Here we are left with just the **weakly acidic salt** so the **solution is weakly acidic**.
- Calculate pH using the weak acid:



10.1.4

Practice: Calculating the pH of the Solution When an Acid and Base React

100 mL of a 0.5 M solution of nitric acid (HNO_3) was added to 75 mL of a 0.37 M solution of sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$) the conjugate base of benzoic acid ($\text{C}_6\text{H}_5\text{COOH} \text{Ka} = 6.6 \times 10^{-5}$). Calculate the pH of the resulting solution.

0.22

0.90

1.12

2.79

10.2 Intro to Buffers & Buffers Problem Type 1

10.2.1

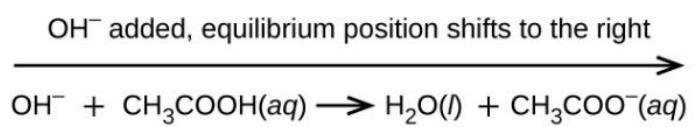
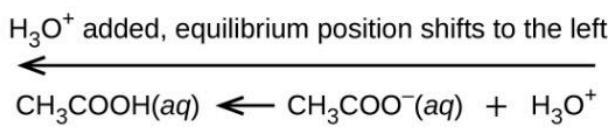
Introduction to Buffers

A **buffer** is a solution that can **resist large changes to pH/pOH**

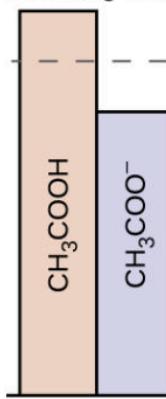
The best ones have ~ **equal [weak acid] and [conjugate base]** OR **[weak base] = [conjugate acid]**

A buffer can even resist large changes in pH when small amounts of either strong acid (H^+) or strong base (OH^-) are added to it!

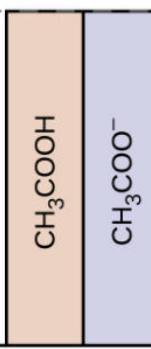
Example:



Buffer solution
after addition
of strong acid



Buffer solution
equimolar in
acid and base



Buffer solution
after addition
of strong base

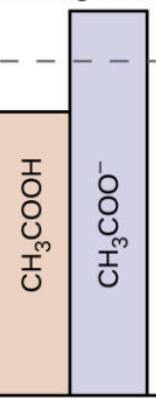


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Buffer Capacity – the extent to which a buffer can resist changes in pH when an acid or base is added.

- A solution with more weak base, $[A^-]$, has a higher buffer capacity for addition of strong acid.
- A solution with more weak acid, $[HA]$, has a higher buffer capacity for addition of strong base.
- **When all of HA or A- has been consumed** and only one conjugate exists, the mixture is no longer a buffer and therefore the **buffering capacity has been exceeded**.

Buffers Problem Type 1

1) Calculate the pH of a buffer solution

You can do this using the way we learned before:



I	0.2M	/		0.1M
C	-x	/	+x	+x
E	0.2-x	/	+x	0.1+x

$$Ka = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$Ka = \frac{x[0.1+x]}{[0.2-x]}$$

$$Ka \approx \frac{x[0.1]}{[0.2]}$$

Given Ka you will be able to solve for x, x=[H⁺], then plug in the [H⁺] to pH=-log[H⁺] and solve for pH!

1) Calculate the pH of a buffer solution

The good news is that for buffers we can use equations to make this much simpler!

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

Henderson-Hasselbalch Equation

pH is the pH of solution

We can get the **pKa** of the buffer from the **Ka** of the buffer that will be provided

[A-] is the concentration of the conjugate base part of the buffer

[HA] is the concentration of the weak acid part of the buffer

$$pK_a = -\log(K_a)$$

$$pK_b = -\log(K_b)$$

$$K_w = (K_a)(K_b) = 1 \times 10^{-14} \quad @ 25^\circ C$$

$$pK_a + pK_b = pK_w = 14 \quad @ 25^\circ C$$

WIZE TIP

When we are given the **Ka** of the buffer we can solve for **pKa** and then plug in the concentrations of the weak acid and its conjugate base directly into the HH equation to solve for pH of the buffer solution!

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

Henderson-Hasselbalch Equation

We said that in a buffer we want ~ equal concentrations of a weak acid and its conjugate base...
Looking at the HH equation, what would happen to that equation if we let $[HA]=[A^-]$?



WIZE CONCEPT

A 1:1 ratio of $[A^-]:[HA]$ will always make $pH=pK_a$.

This is why we want to build a buffer with a pK_a close to the desired pH

Note: There is another form of the HH equation we can use if the buffer is made of a weak base and its conjugate acid (this one is used much less commonly).

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

10.2.3

Example: Buffers Problem Type 1

A buffer solution is made of 0.1mol of CH_3COOH and 0.2mol of NaCH_3COO in 1L of solution. What is the pH of the solution? $K_a(\text{CH}_3\text{COOH})=1.8\times 10^{-5}$

10.3 Buffers Problem Type 2

10.3.1

Buffers Problem Type 2

2) Calculation of the pH of a buffer solution after addition of a small amount of strong acid

The strong acid will react completely with the conjugate base of the buffer



- Reaction goes to completion
- Plug in the initial moles values into the ICE table to find the final moles.

Next: Take the **final moles value of the conjugate acid and base** and plug those values into the HH equation to solve for pH:

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

10.3.2

Example: Buffers Problem Type 2

Our buffer solution is made of 0.1mol of CH_3COOH and 0.2mol of NaCH_3COO in 1L solution.

$$\text{Ka}(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

If we added 75mL of 0.1M HNO_3 (aq), what is the pH of our buffer solution?

Is HNO_3 a base or an acid? _____

Is it strong or weak? _____

Will there be complete or incomplete dissociation? _____

1) Write out the chemical reaction for the dissociation of HNO_3 . Solve for moles of H^+ .

2) Write the chemical reaction that shows how the buffer would react with these added $[\text{H}^+]$ ions:

3) You can plug in the final moles values of A^- and HA in the Henderson Hassalbalch equation to solve for pH:

10.4 Buffers Problem Type 3

10.4.1

Buffers Problem Type 3

3) Calculation of the pH of a buffer solution after addition of a small amount of strong base

The strong base will completely react with the acid part of the buffer



- Reaction goes to completion.
- Put the initial moles values into an ICE Table to solve for the final moles.

Next: Take the **final moles value of the conjugate acid and base** and plug those values into the HH equation to solve for pH:

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

10.4.2

Example: Buffers Problem Type 3

Our buffer solution is made of 0.1mol of CH_3COOH and 0.2mol of NaCH_3COO in 1L solution.

$$\text{Ka}(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

If we added 0.02 mol of NaOH to our solution what is the pH of our solution now?

Is NaOH a base or an acid? _____

Is it strong or weak? _____

Will there be complete or incomplete dissociation? _____

1) Write out the chemical reaction for the dissociation of NaOH. Solve for the moles of OH^- .

2) Write the chemical reaction that shows how the buffer would react with these added OH^- ions:

3) Plug in the final moles values into the Henderson Hassalbalch equation to solve for pH:

10.4.3

Practice: Calculate the pH of a Buffer Solution

A buffer is prepared by adding 0.021 moles of HI to 250mL of 0.71M of $(CH_3)_2NH(aq)$. What is the pH of this buffer? $K_b((CH_3)_2NH(aq))=5.4\times 10^{-4}$ (Assume there is no change in volume)

5.5

6.7

9.9

11.6

12.4

10.5 Foming Buffers

10.5.1

Forming Buffers

 WIZE TIP

Exams commonly ask questions about which combinations of molecules could form buffers!

To determine if compounds will form a buffer we need to look for a few things:

Do we have a weak acid and its conjugate base? If we do, this will form a buffer!

If we have a strong acid/base reacting with a weak acid/base, we might form a buffer:

1. If we react an **equal amount** of **strong acid/base** with **weak base/acid** then there will be a **chemical reaction** but **no buffer** since there is no weak substance left

Example:



2. If we react a **strong acid/base in excess** with a **weak base/acid** and **of the strong substance** then there will be a **chemical reaction** but **no buffer** because there is excess of the strong substance and no weak substance left

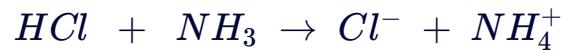
Example:



3. If we react a **strong acid/base** with a **weak base/acid** and have **less of the strong substance** then there will be a **chemical reaction** and there will be a **buffer** since the strong substance will

completely react, leaving us with the weak substance and its conjugate=buffer

Example:



There are 2 methods of preparing buffers:

1. If sources of **both HA and A⁻** are readily available, then an appropriate amount of each component can be measured out to give the buffer solution.
2. If **only one of the conjugate acid-base pair** is available (i.e. either HA or A⁻), a controlled amount of a strong acid or a strong base can be added to the solution of the available reagent which will result in the formation of HA and A⁻ needed to achieve the desired buffer ratio.

10.5.2

Example: Identifying Buffers

Determine if the following mixtures would constitute as buffers.

- a) A solution containing acetic acid and sodium acetate.

b) A solution containing hydrocyanic acid and ammonia.

10.5.3

Examples: Forming Buffers

Do the following combinations of molecules form a buffer solution?

a) 1M CH_3COO^- with 0.8M HCl

CH_3COO^- : acid/base: _____, weak/strong: _____

HCl: acid/base: _____, weak/strong: _____

Forms buffer? (write out chemical equation)

Do the following combinations of molecules form a buffer solution?

b) 2M HCl and 1M HBr

HCl: acid/base: _____, weak/strong: _____

HBr: acid/base: _____, weak/strong: _____

Would this combination form a buffer?

Do the following combinations of molecules form a buffer solution?

c) 1M NH_3 and 0.8M NH_4^+

NH_3 : acid/base: _____, weak/strong: _____

NH_4^+ : acid/base: _____, weak/strong: _____

Would this combination form a buffer?

10.6 Preparing Buffers with Desired pH

10.6.1

Example: Preparing a Buffer With a Desired pH

How many moles of NaCH_3COO should be added to 700mL of a 0.15M of CH_3COOH to get a pH of 4.8? Assume no volume change. $\text{pK}_a=4.75$

10.7 Titration Curves

10.7.1

Introduction to Titrations

Acid-base titrations are **neutralization reactions** between a **titrant** (solution in the buret) and **analyte** (solution in the flask).

WIZE CONCEPT

Titrations always involve an acid reacting with a base!

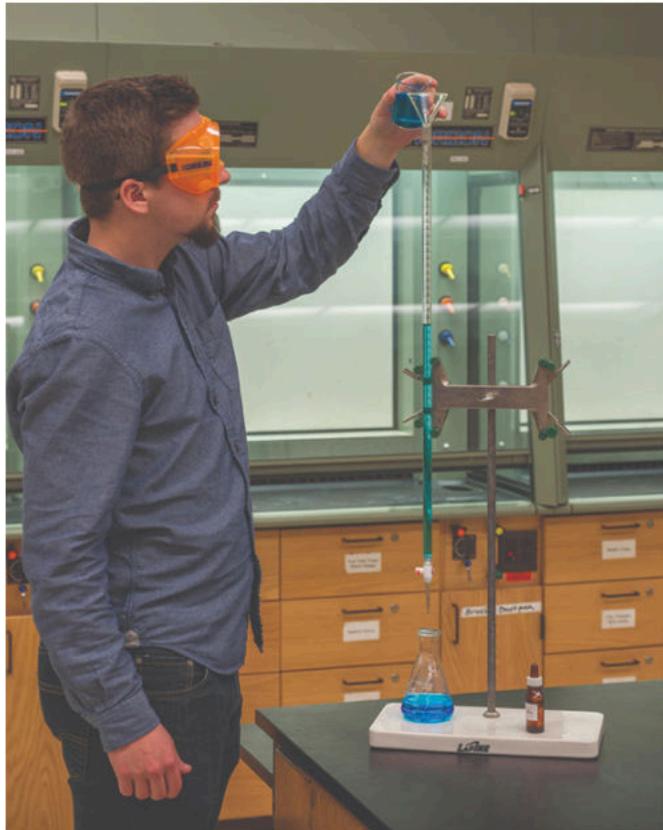
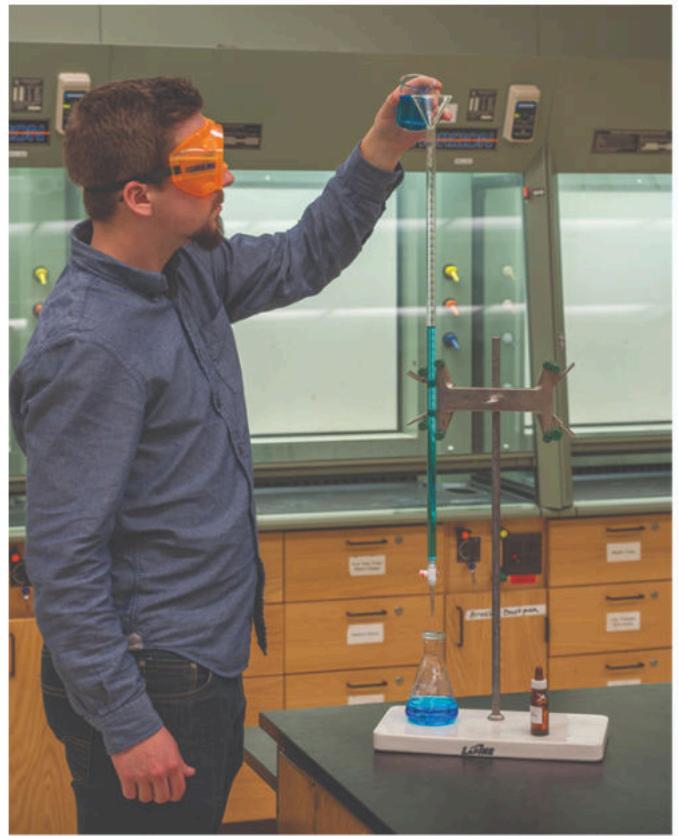


Photo by Rice University / CC BY

Titrant

- Solution in the buret
 - We control the amount we add of the titrant to the flask
 - We know its volume, concentration, and identity
- Example:* 1M 100mL NaOH
- It is usually a strong acid or base



Analyte

- Solution in the flask
- It is the unknown (we don't know its concentration, identity, or if it is weak or strong)
- We do know its volume (can easily measure its volume in the flask) and its pH (we can simply use a pH meter to measure this in the flask)
 - The other way to know if there's a pH change in the flask is if we see a visual change in color
 - **Indicators** help to indicate this pH change by changing the color inside the flask
 - When the color changes, we call this an **end-point**.

WIZE CONCEPT

We do titrations (where we add small amounts of titrant to the analyte) to determine the unknown concentration of an acid or a base!

10.7.2

Labeling a Titration Curve

A plot showing the pH of the solution as a function of the quantity of acid or base added is known as a **titration curve**.

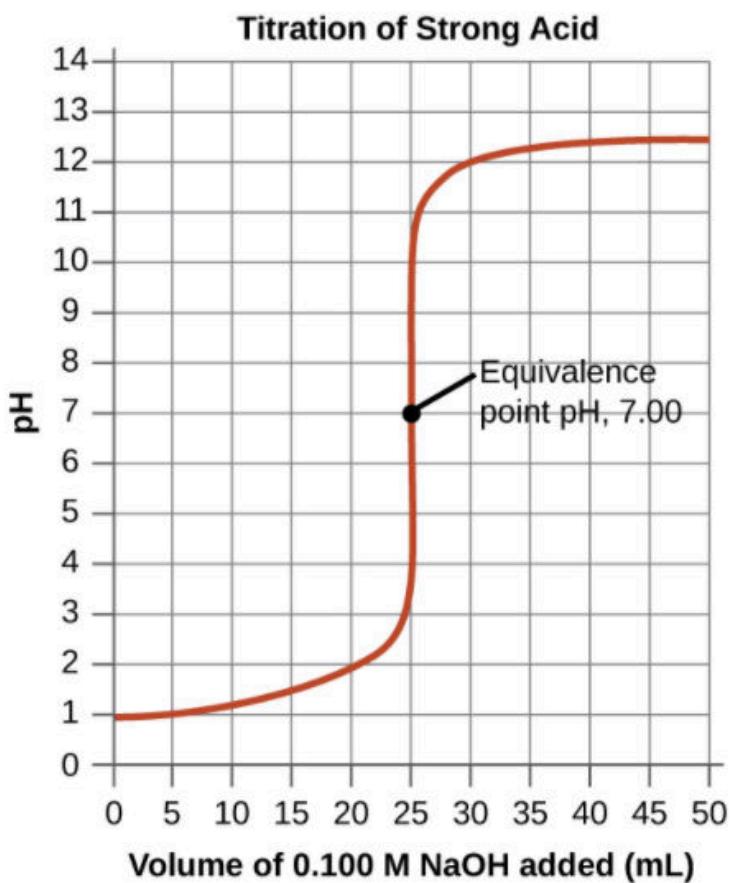


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The titrant (substance in the buret that is being added to the analyte in the flask slowly overtime) is:

What is the volume for the equivalence point? _____

What is the volume for the half equivalence point? _____

WIZE CONCEPT

@ Half-Equivalence Point: $[HA] = [A^-]$ and moles of acid=moles of conjugate base

- Exactly half of the initial amount of weak species has been reacted by the addition of a strong base or acid
- Remember according to the Henderson Hassalbalch equation: $pH = pK_a - \log \frac{[conjugate\ base]}{[conjugate\ acid]}$
- When the $[HA]=[A^-]$ how are pH and pKa related?
 - $\log 1=0$ so **pH=pKa of analyte**

@ Equivalence Point: $[HA] = [OH^-]$ added and moles of acid=moles of base

- Enough titrant has been added to completely neutralize ALL of the unknown
- In other words, the acid and base have completely reacted together so there is no more acid or base left.

Finally, the **pH @ Equivalence Point** ($pH=7$, $pH < 7$, or $pH > 7$) is determined by the acidity/basicity of the salt produced

- Strong acid and strong base → pH @ equivalence point will be neutral ($=7$)
- Strong acid and weak base → pH @ equivalence point will be acidic (<7)
- Weak acid and strong base → pH @ equivalence point will be basic (>7)

Titration Curves

1. Strong Acid – Strong Base ($\text{HCl}_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$)

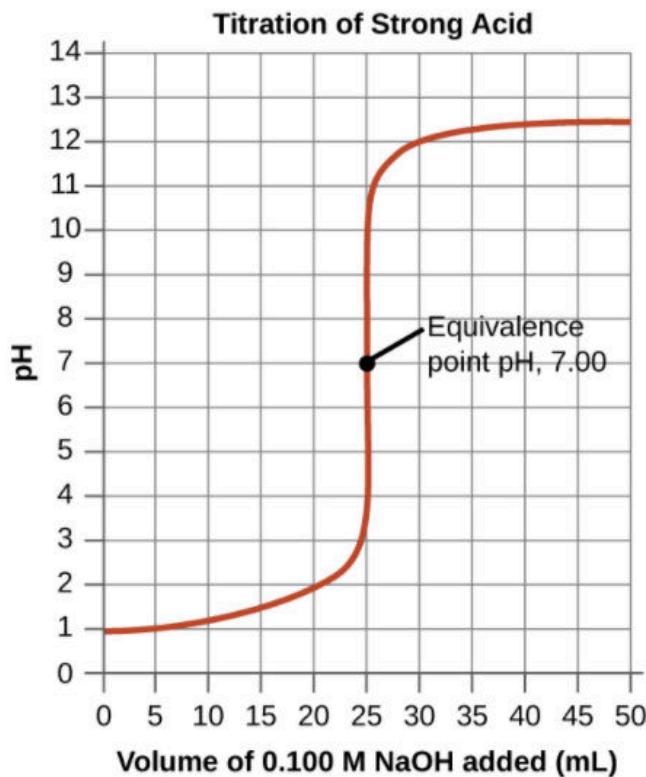


Photo by Rice University / CC BY

- pH is low initially
- As base is added, the pH increases slowly.
- The pH rises steeply when the moles of OH^- nearly equals the moles of H_3O^+
- pH _____ 7 at equivalence point
- The additional drop of base neutralizes the tiny excess acid and introduces a tiny excess of base
- Then, pH increases smoothly as more base is added.

2. Weak acid – Strong base Titration ($\text{CH}_3\text{COOH}_{(\text{aq})}$ with $\text{NaOH}_{(\text{aq})}$)

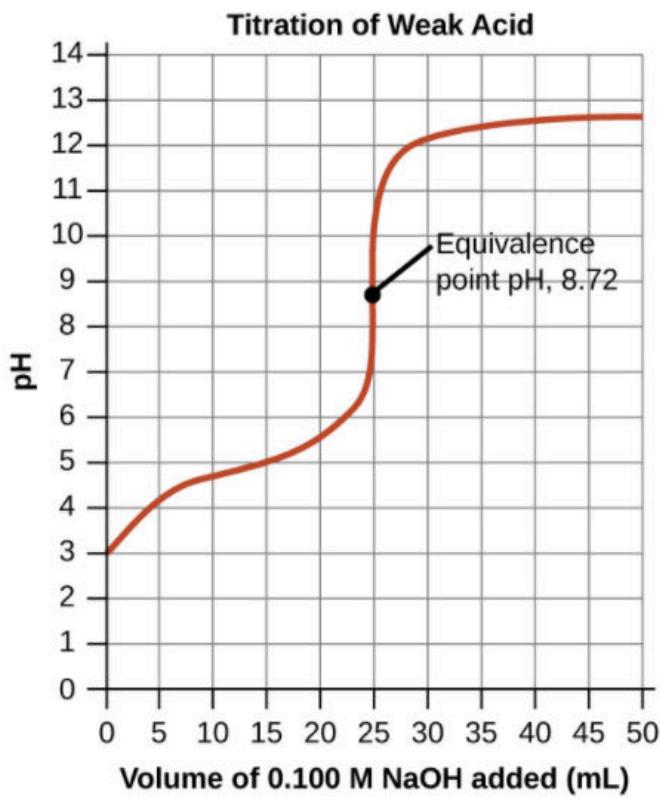
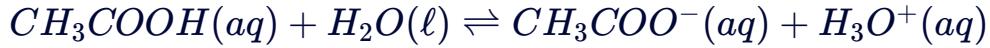


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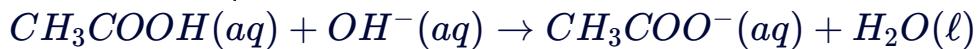
- In a weak acid – strong base titration: pH _____ 7 at the equivalence point
- Past the equivalence point: pH determined by the $[\text{OH}^-]$ from the excess strong base. You need the total volume of the solution to determine $[\text{OH}^-]$

Calculating pH at different points in the titration

At the start: solution of the weak acid, CH_3COOH ; use ICE table and K_a to determine pH

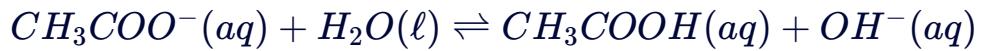


Between the start and equivalence point: buffer region due to presence of both CH_3COOH and CH_3COO^- ; determine moles of acid left unreacted and moles of base produced. Use Henderson–Hasselbach equation to solve for pH.



At half equivalence point: pH = pKa

At equivalence point: all CH₃COOH has been converted to CH₃COO⁻; the pH is controlled by the acetate ion, and is thus basic.



Past the equivalence point: pH determined by the [OH⁻] from the excess strong base. You need the total volume of the solution to determine [OH⁻]

3. Weak base –Strong acid Titration: (NH₃ and HCl)

Draw the titration curve where HCl(aq) is the titrant and being added in gradually.

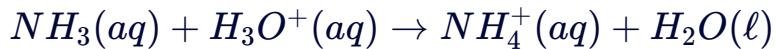
- In a weak base – strong acid titration: pH _____ 7 at the equivalence point
- Past the equivalence point: pH determined by the [H₃O⁺] from the excess strong acid

Calculating pH at different points in the titration

At the start: solution of the weak base, NH₃; use ICE table and K_b to determine pH

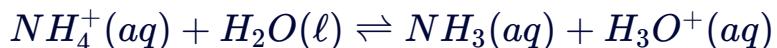


Between the start and equivalence point: buffer region due to presence of both NH₃ and NH₄⁺ determine [NH₃] left unreacted and [NH₄⁺] produced; use Henderson-Hasselbach equation to determine pH



At half equivalence point: pH = pK_a of NH₄⁺

At equivalence point: all NH₃ has been converted to NH₄⁺; use K_a of NH₄⁺ to determine [H₃O⁺]



Past the equivalence point: pH determined by the [H₃O⁺] from the excess strong acid

10.7.4

Practice: Equivalence Point

For which type of titration will the pH be basic at the equivalence point?

Strong acid vs. strong base.

Strong acid vs. weak base.

Weak acid vs. strong base.

All of the above.

None of the above.

10.8 Titration Problems

10.8.1

Example: Solving for the pH at Equivalence Point

What is the pH at the equivalence point when 40.00 mL of 0.89 M Benzoic acid ($K_a = 6.3 \times 10^{-5}$) is titrated with 1.0 M NaOH?

Example: Everything You Could Be Asked About Titrations

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

- a) What is the concentration of ammonia in the original sample?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

b) What is the initial pH of the sample, before adding acid?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

c) What is the equivalence point pH?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

d) Solve for pH when 42.86mL of HCl has been added to the sample

hint: what point does this represent on a titration curve?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

e) What is the pH after 71.43 mL of hydrochloric acid has been added to the sample?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

f) What is the pH after 90mL of HCl has been added?

A 200.0 mL sample of ammonia ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.700 M hydrochloric acid. It requires 85.71 mL of hydrochloric acid to reach equivalence point.

g) Draw the titration curve

10.9 Indicators

10.9.1

Indicators

An **indicator** is a weak acid or base added in a very small quantity to the titration solution before the experiment begins. Usually they are **weak acids**.

The indicator has a special property: its acid and conjugate base forms appear as different colours in solution

Example:



WIZE CONCEPT

The pKa value of the chosen indicator should be close to the pH of the solution at the equivalence point (ideally within 1 pH unit of the equivalence point)

We want the indicator to signal a colour change close to the equivalence point.

When the pH of the solution=pKa of the indicator, the indicator's acid and conjugate base components will have an equal concentration $[HIn]=[In^-]$ and we will see a mixture of the two colors!

Example:

In our example above, we'd see a **red** colour

Equivalence Point vs Endpoint

Equivalence point: moles of H^+ =moles of OH^-

End point: when we see a colour change because of the indicator

Example:

Look at methyl orange in the table below. Indicate an endpoint and a possible equivalence point.

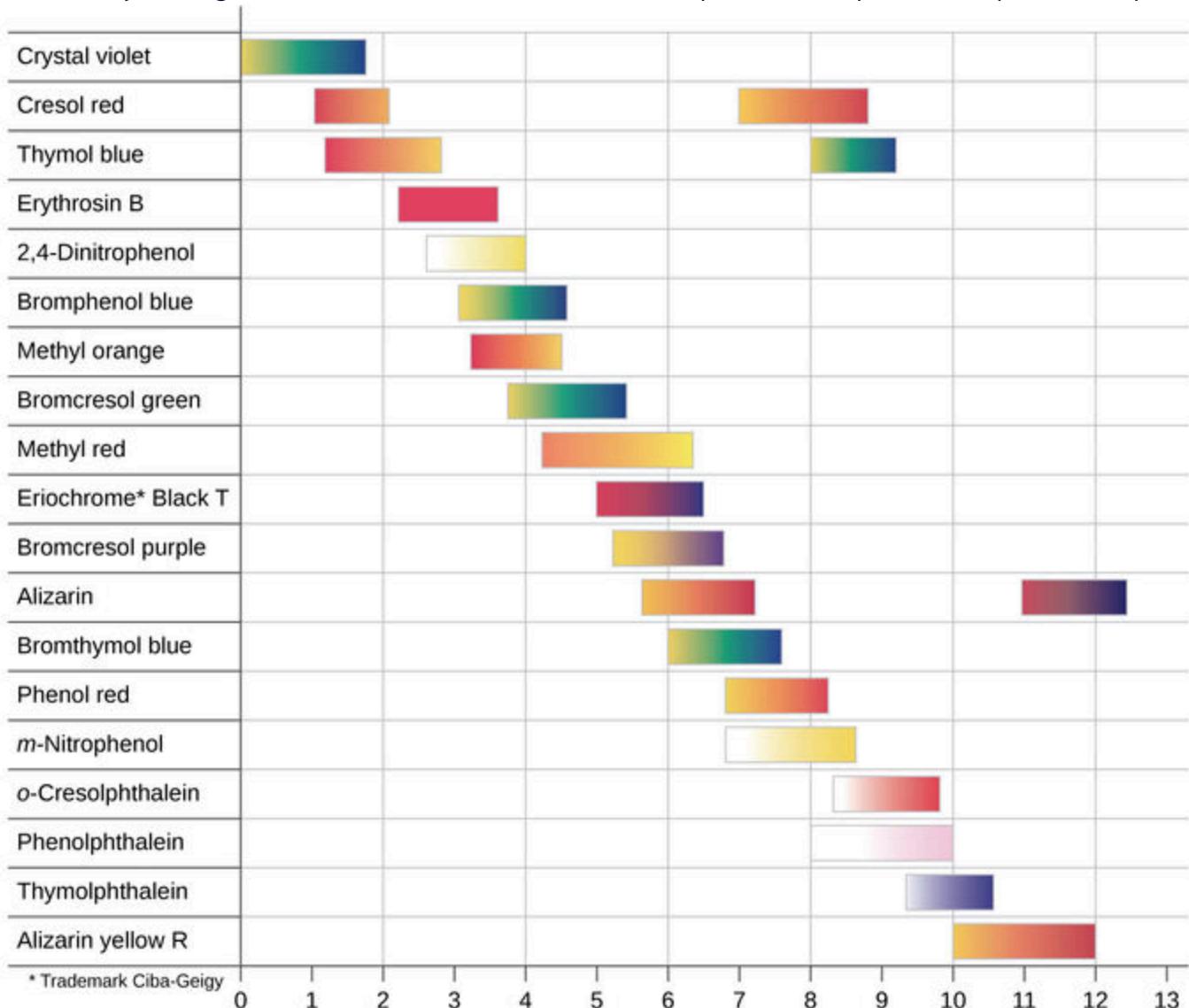


Photo by OpenStax / CC BY



1) When $\text{pH} = \text{pK}_a$ of indicator:

- $[HIn] = [In^-]$
 - red + blue \rightarrow we'd see !

2) When $\text{pH} < \text{pK}_a$

- $[HIn] > [In^-]$
 - we'd see !

3) When $\text{pH} > \text{pK}_a$

- $[HIn] < [In^-]$
 - we'd see !

10.9.2

Practice: Indicators

The indicator cresol red has $K_a = 5.0 \times 10^{-9}$. Over what approximate pH range does it change colour?

6.3 to 8.3



7.3 to 8.3



7.3 to 9.3



7.8 to 10.7

