Chapter 17

Acid – Base Equilibria
&
Solubility Equilibria

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)]

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

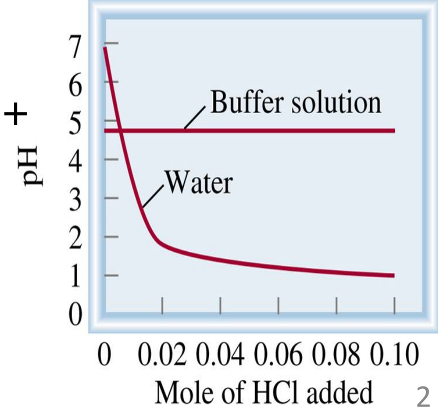
When small amounts of a strong acid or base are added:

- Acidic species in buffer neutralizes added OH^-

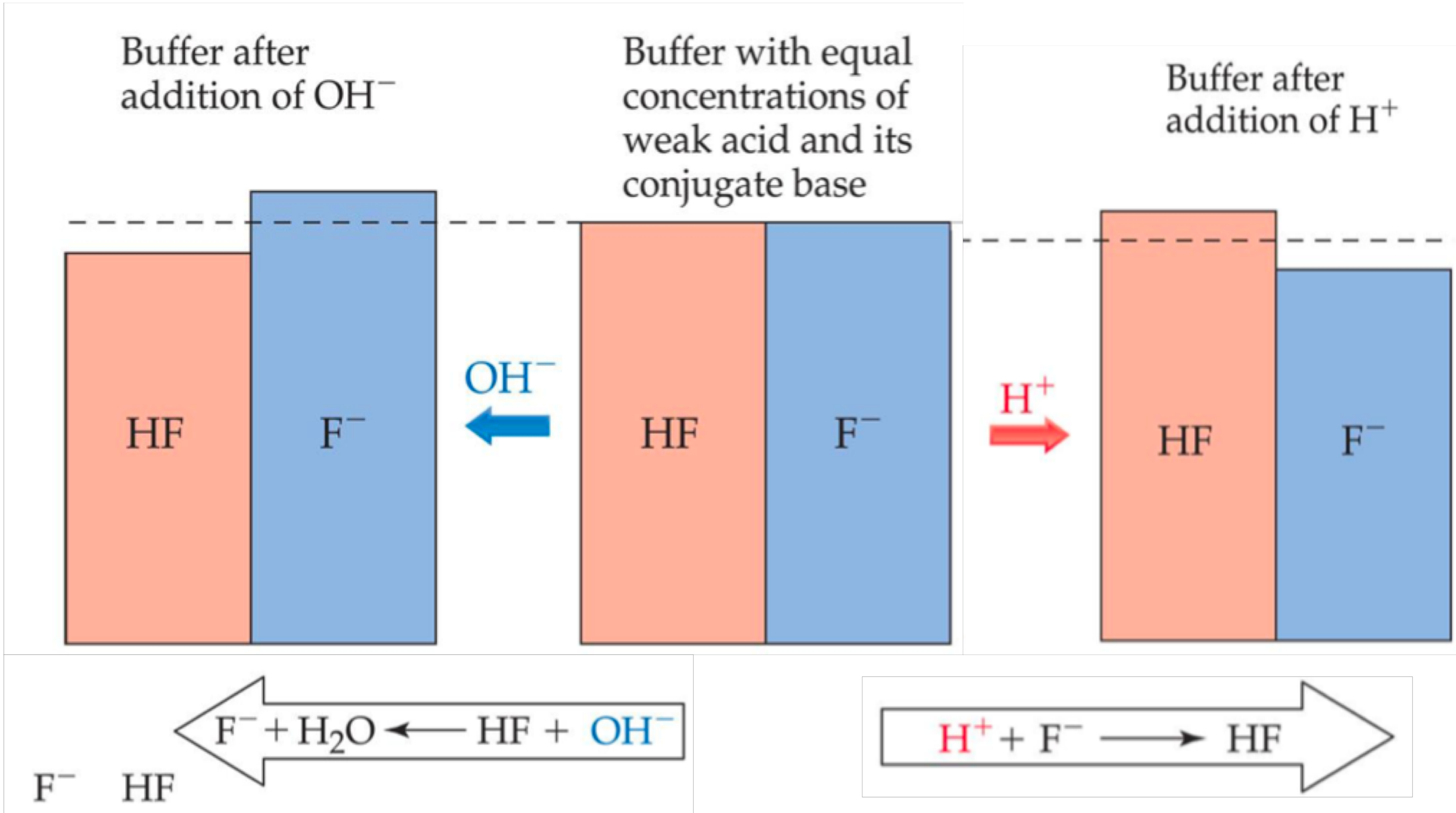
$$HA + OH^- \rightleftharpoons H_2O + A^-$$

- 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

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

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?

$K_a = 7.2 \times 10^{-4}$

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?

$K_a = 7.2 \times 10^{-4}$

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? $K_a = 1.4 \times 10^{-4}$; 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 $pH = pK_a$

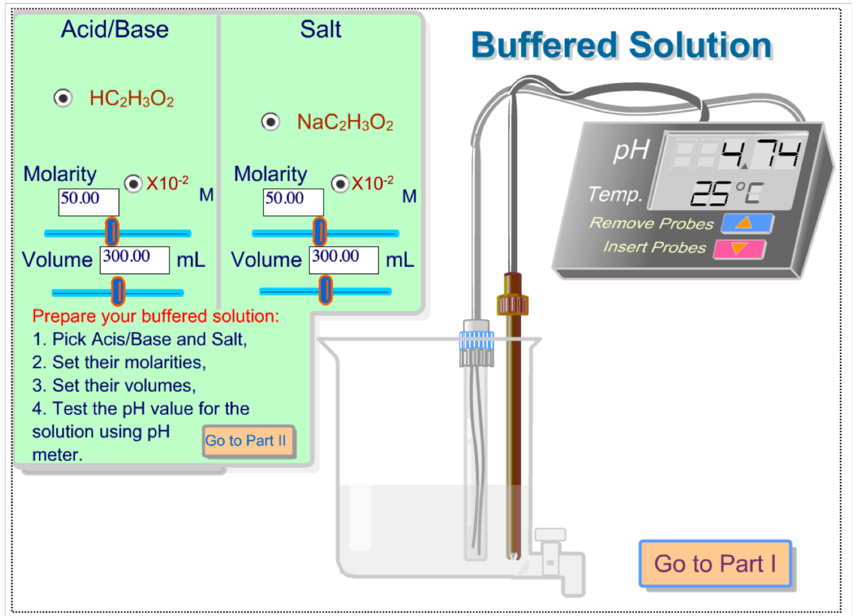
$$\boxed{\mathbf{pH = pK_a + \cancel{\log \frac{[A^-]}{[HA]}}}}$$

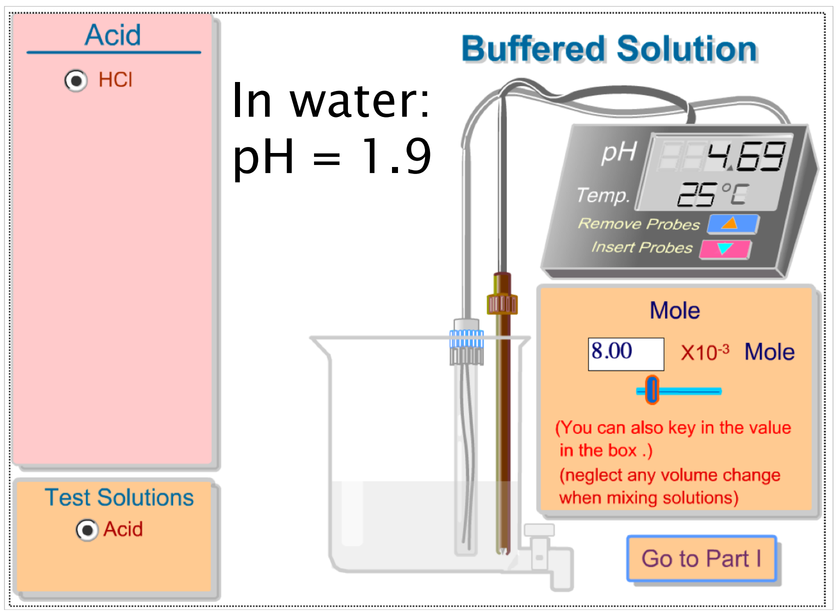
$\log(1) = 0$

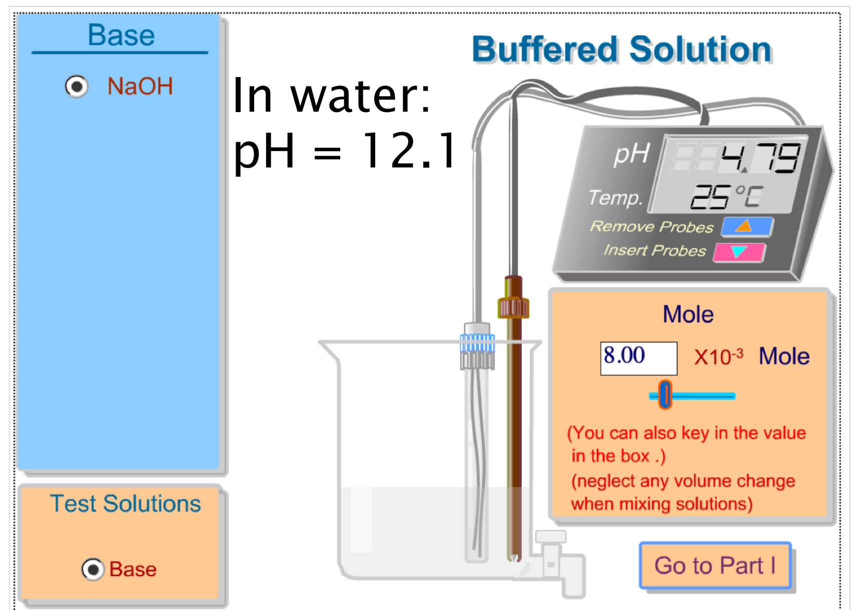
- Buffer generally usable withing ± 1 pH unit of the pK_a

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.







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

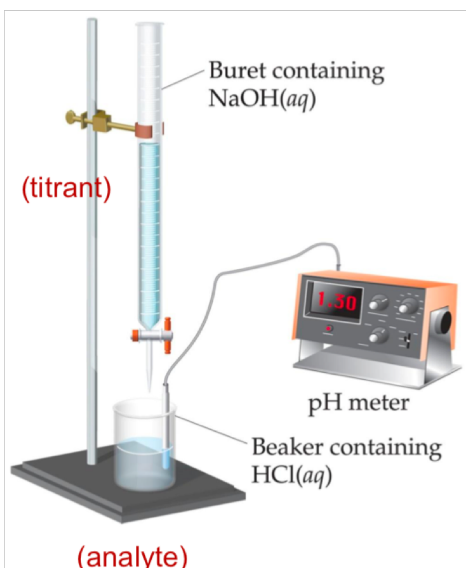
(b) Calculate the pH after 0.040 mol HCl is added. A: 4.69

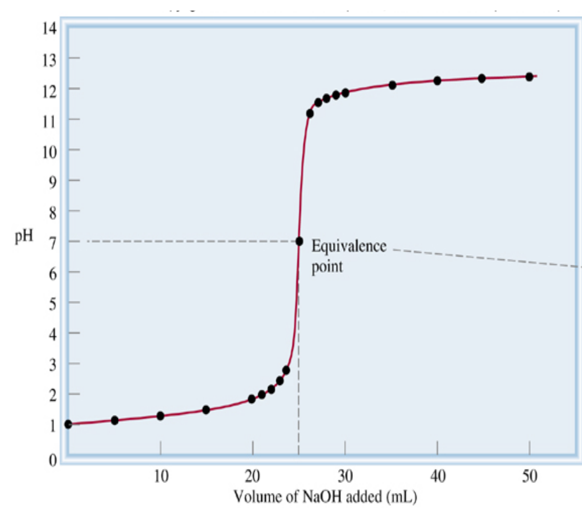
(c) Calculate the pH after 0.040 mol NaOH is added. A: 4.80

Titration

A technique where a known concentration of acid (or base) is added to a solution of base (or acid).

- Used the determine the concentration of an unknown
- In CHM 101 we looked at <u>strong</u> acid/base systems
  - No equilibrium
  - Equivalence point is pH 7
- Indicators or pH meters are used to determine the equivalence point.



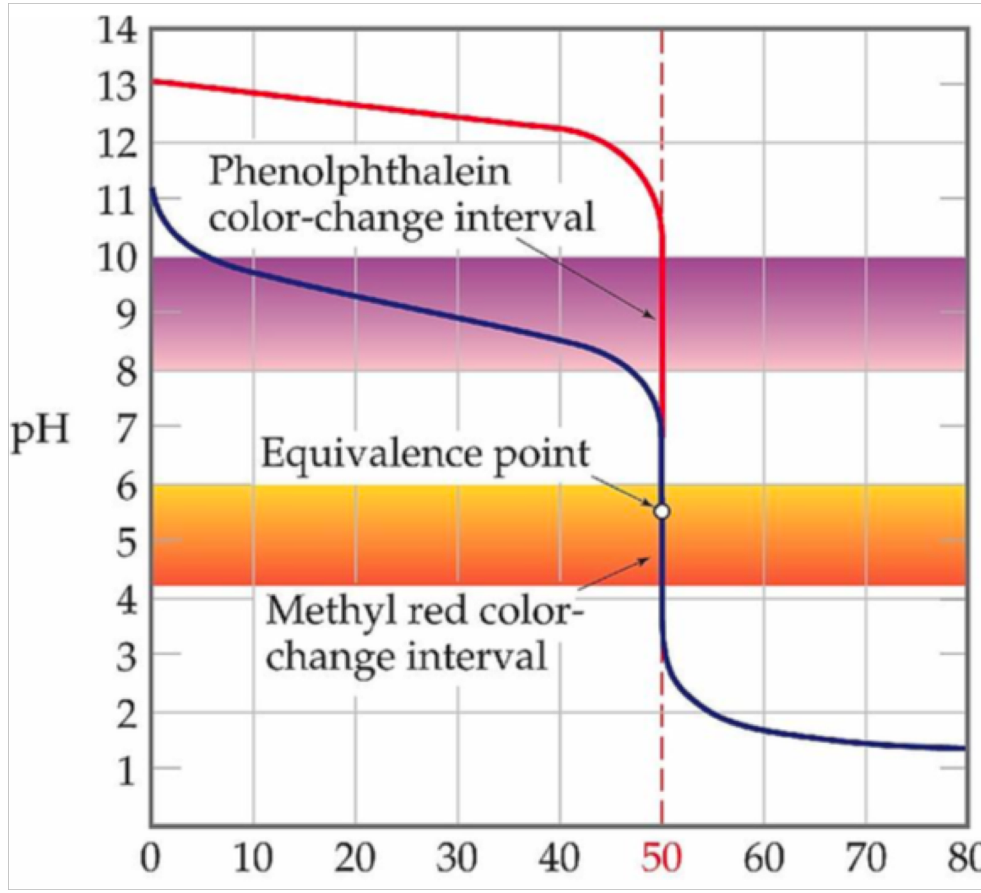


Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Titration Terminology

Equivalence Point: Point at which the stoichiometric amount of acid and base are equal.

End Point: Point in the titration where the indicator changes color.



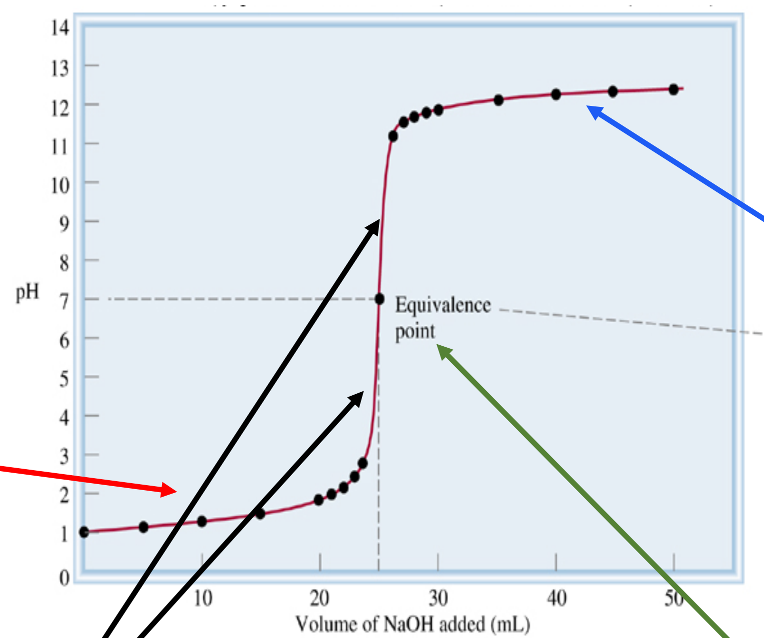
Solving More Complex Titration Problems

1. **Read the question carefully to see what it is asking**
   - pH at a particular point
   - Moles or molarity of original solution
   - pH or volume at equivalence point
2. **Identify all reactants and products**
   - Write the balanced equation
   - Determine the predominant products based on amounts given
   - Identify whether the solution is acidic or basic
3. **Determine whether it is an equilibrium process**
   - You will have at most one equilibrium
   - Strong acids/bases – direct calculations from molarity
   - Weak acids/bases – equilibrium calculations
4. **Volume increases during titrations so watch for dilution factors**

Titration of a Strong Acid with a Strong Base

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

From the start of the titration to near the endpoint, the pH increases slowly



As more base is added, the increase in pH again levels off

Just before (and after) the equivalence point, the pH increases rapidly

At the equivalence point, moles acid = moles base
Solution contains only water and salt (neutral)

Strong Acid/Strong Base Calculations

In the titration of 25.0mL of 0.100M KOH with 0.100M HNO_3, determine the pH:

(a) At the start of the titration (no acid added) A:13.0

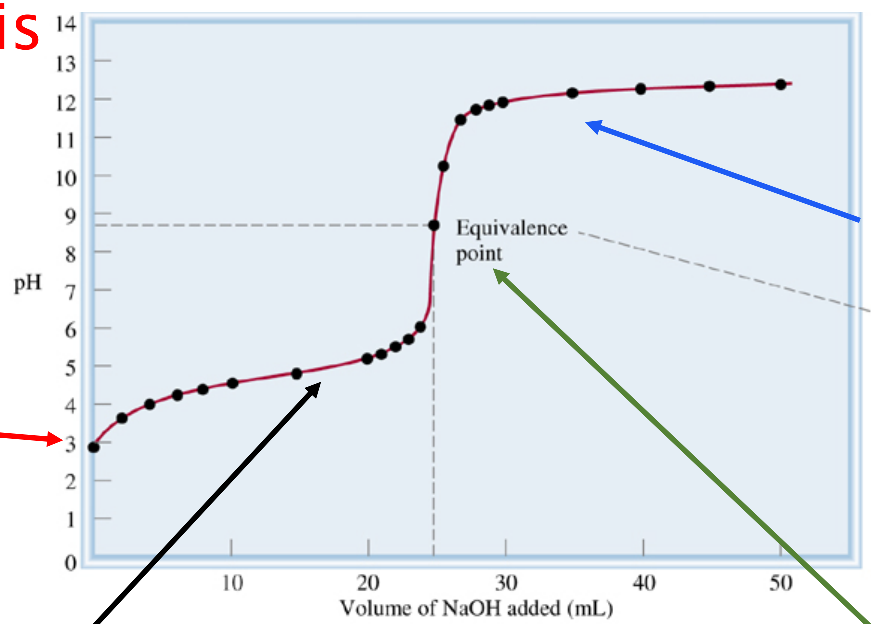
(b) When 24.9mL acid has been added A: 10.3

(c) When 25.1mL acid has been added A: 3.7

Titration of a Weak Acid with a Strong Base

$$NaOH(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$$
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Initially there is only the weak acid; pH depends on concentration & K_a

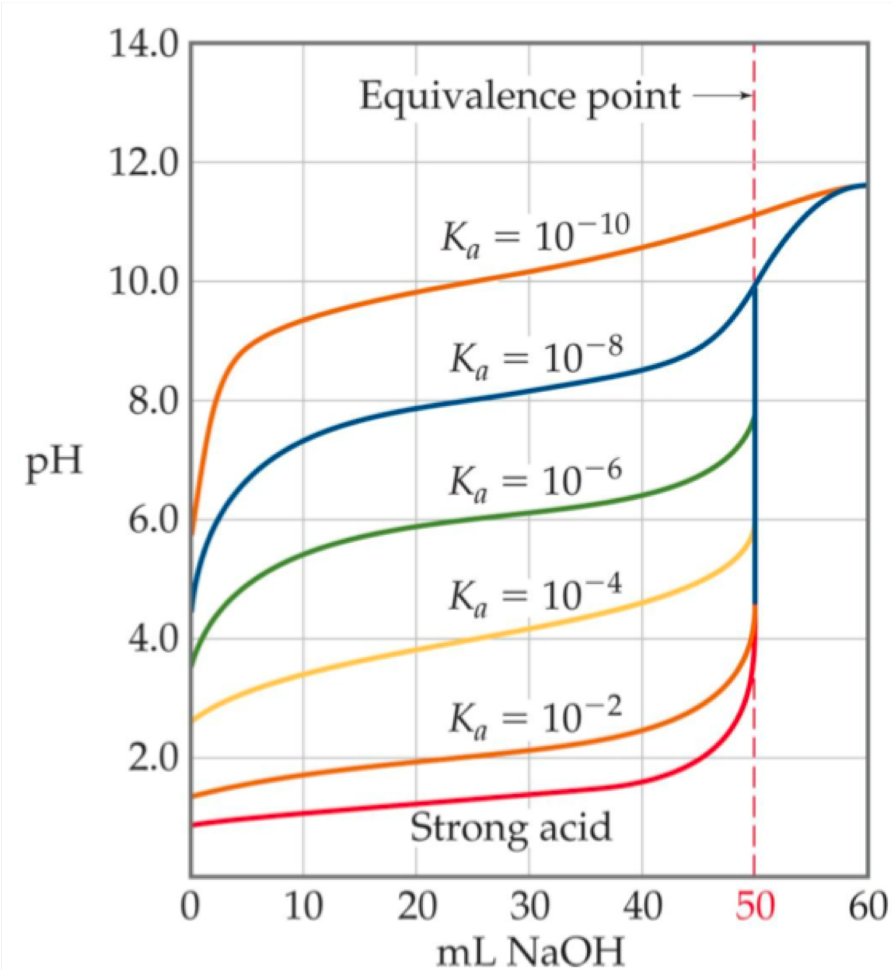


After the equivalence pt., pH depends on concentration of excess strong base

Before the equivalence pt., the solution is a buffer – it contains the weak acid & its conjugate base

At the equivalence pt. (moles acid = moles base) pH is >7 because the conjugate base of the acid affects the pH

Titration of a Weak Acid with a Strong Base



With weak acids:

- Initial pH is higher
- pH changes near the equivalence point are more subtle (smaller)
- pH > 7 at equivalence point due to the formation of a basic salt (conjugate base of weak acid; ex: CH_3COONa

Weak Acid/Strong Base Calculations Things to Keep in Mind

1. **Acid/Base titration always gives a salt & water**
   - $HA + OH \rightleftharpoons A^- + H_2O$
2. **Initial pH only depends on the weak acid**
   - K_a & concentration
3. **Addition of base up to just before equivalence point essentially forms a buffer solution**
   - Contains weak acid & its conjugate base (salt)
   - Can use Henderson-Hasselbalch to determine pH
   - Determine moles of A^- & HA, then use total volume to calculate concentrations
   - Moles of salt will equal moles of base added because all added base will have been neutralized to form salt
4. **Volume increases during titrations so watch for dilution factors**

Weak Acid/Strong Base Calculations Things to Keep in Mind con't

4. **At the equivalence point, all acids & bases are neutralized and the solution only contains the salt**
    - The salt will be basic – it is the product of a weak acid & a strong base
    - Main reaction is now hydrolysis of the salt
    - $A^- + H_2O \rightleftharpoons HA + OH^-$
    - Since the solution is basic – use K_b
    - Can use moles of either acid or base to determine moles of salt formed.
    - Use total volume to get concentration.
5. **After the equivalence point, there is only the excess strong base**
    - pH will depend on concentration of excess strong base – moles not neutralized & total volume

Weak Acid/Strong Base Calculations

When 100.0 mL of 0.10 M HNO_2 are titrated with a 0.10 M NaOH solution, what is the pH at the equivalence point? K_a $HNO_2 = 4.5 \times 10^{-4}$

start (moles) 0.010 0.010

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

end (moles) 0.0 0.0 0.010

Final volume = 200 mL ⇨ $[NO_2^-] = \dfrac{0.010}{0.200} = 0.050\ M$

Use K_b

$K_b = 2.2 \times 10^{-11}$

Hydrolysis of basic salt $NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HNO_2\,(aq)$

	NO_2^-	OH^-	HNO_2
Initial (M)	0.050	0.00	0.00
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.050 - \cancel{x}$ 0	x	x

$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.050} = 2.2 \times 10^{-11}$$

$x = 1.05 \times 10^{-6} = [OH^-]$

pOH = 5.98

pH = 14 – 5.98 = 8.02

Weak Acid/Strong Base Calculations

35.0mL of 0.150M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) was titrated with 0.150M NaOH. Determine the pH:

a.) At the start of the titration A: 2.78

b.) When 20.0mL of 0.150M NaOH has been added A:4.88

c.) At the equivalence point A: 8.86

d.) When 50.0mL of 0.150M NaOH has been added A: 12.42

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Weak Acid/Strong Base Calculations

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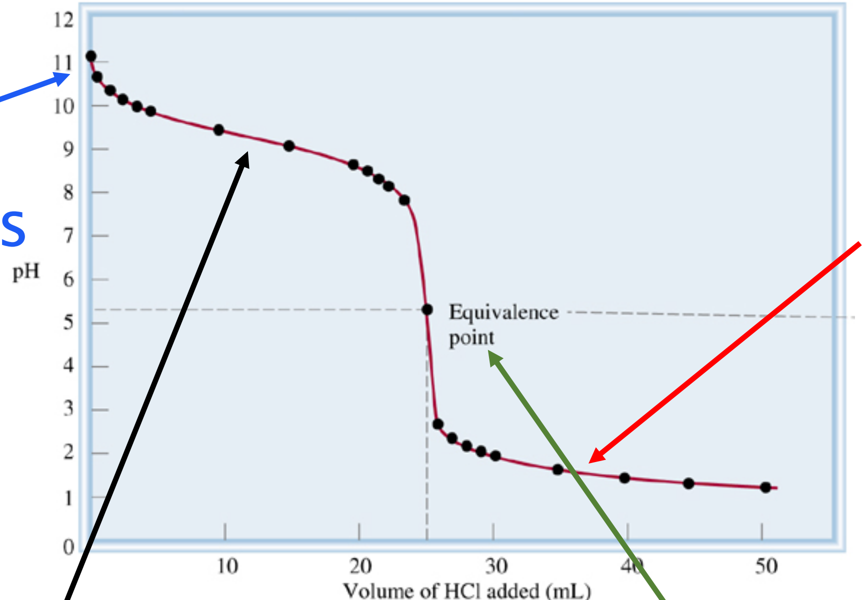
d.) When 50.0mL of 0.150M NaOH has been added A: 12.42

Titration of a Weak Base with a Strong Acid

$$HCl(aq) + NH_3\ (aq) \rightleftharpoons NH_4^+\ (aq) + Cl^-(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3\ (aq) + H_3O^+(aq)$$

Initially there is only the weak base; pH depends on concentration & K_b



After the equivalence pt., pH depends on concentration of excess strong acid

Before the equivalence pt., the solution is a buffer – it contains the weak base & its conjugate acid

At the equivalence pt. (moles acid = moles base) pH is < 7 because the conjugate acid of the base affects the pH

Weak Base/Strong Acid Calculations

30.0mL of 0.0300M NH_3 ($K_b = 1.8 \times 10^{-5}$) was titrated with 0.0250M HCl. Determine the pH:

a.) At the start of the titration A: 10.87

b.) When 20.0mL of 0.0250M HCl has been added A: 9.12

c.) At the equivalence point A: 5.50

d.) When 37.0mL of 0.025M HCl has been added A: 3.43

Weak Base/Strong Acid Calculations

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Weak Base/Strong Acid Calculations

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c.) At the equivalence point A: 5.50

Weak Base/Strong Acid Calculations

30.0mL of 0.0300M NH_3 ($K_b = 1.8 \times 10^{-5}$) was titrated with 0.0250M HCl. Determine the pH:

d.) When 37.0mL of 0.025M HCl has been added A: 3.43

Acid-Base Indicators

Chemical added during a titration to cause a color change at a particular pH allowing the user to detect the endpoint.

Things to consider when choosing an indicator:

Example: titration of CH_3COOH with NaOH

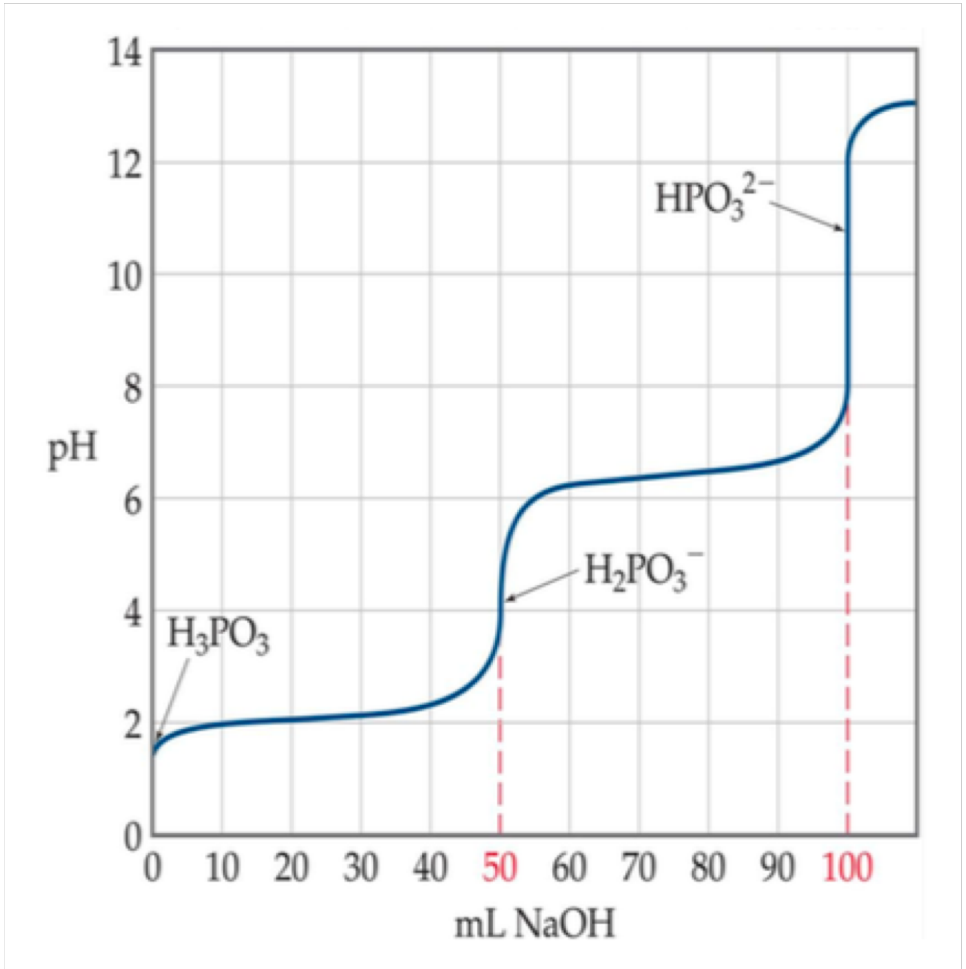
- What kind of titration is it? Weak acid with strong base
- What kind of salt is formed? Basic salt
- What happens to pH due to hydrolysis? Salt is basic so pH > 7.0

TABLE 17.1 Some Common Acid-Base Indicators

	Color		
Indicator	In Acid	In Base	pH Range*
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

Titrations of Polyprotic Acids



The titration of a polyprotic acid with a base will give an equivalence point for each acidic proton.