Chemistry 12

Acid-Base Equilibrium VII

IV 16-17
pg 154-163

Name:
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1. **Titrations**
2. **Indicators**

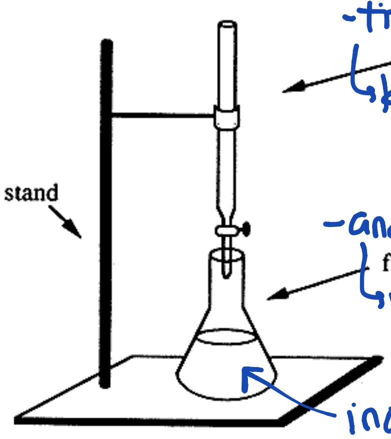
Titrations

unknown → and therefore [ ]

Titration is a form of volumetric analysis where the number of moles of solute in a solution is determined by adding a sufficient volume of another solution of known concentration to just produce a complete reaction.

known

- The reaction is completed when the number of moles of H_3O^+ equals the total number of moles of OH^- - this is called the **equivalence point** or **stoichiometric point** of the titration.
- An **indicator** is used that will indicate when the equivalence point has been reached by changing colour at or very near the pH associated with the equivalence point.



We will be dealing with 3 scenarios:

1. $SA + SB$

   ex. $HCl + NaOH \rightarrow H_2O + \overbrace{NaCl}^{neutral}$

2. $WA + SB$

   ex. $CH_3COOH + NaOH \rightarrow H_2O + \overbrace{NaCH_3COO}^{WB\,(basic)}$

3. $SA + WB$

   ex. $HCl + NH_3 \longrightarrow \overbrace{NH_4^+}^{WA\,(acidic)} + Cl^-$ (spec.)

(Chemistry 11) Example 1: A student standardizing a solution of NaOH finds that 28.15 mL of that solution is required to neutralize 25.00 mL of a 0.1072 M standard solution of HCl. Calculate the $\boxed{[NaOH]}$.

known unknown

- Write the balanced equation.

$$\underset{\substack{0.1072M \\ 25.00mL}}{HCl} + \underset{\substack{?M \\ 28.15mL}}{NaOH} \longrightarrow H_2O + NaCl$$

- What is the concentration of NaOH?

$$25.00\,\cancel{mL}_{HCl} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{0.1072\,\cancel{mol}_{HCl}}{1\,\cancel{L}} \times \frac{1\,mol_{NaOH}}{1\,mol_{HCl}} = 2.680\times10^{-3}\,mol_{NaOH}$$

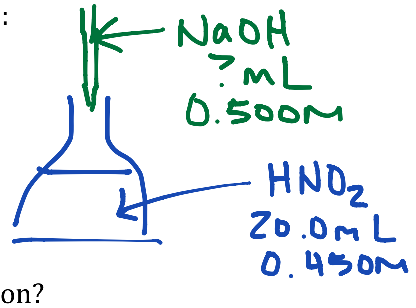
$$\frac{2.680\times10^{-3}\,mol_{NaOH}}{28.15\,\cancel{mL}} \times \frac{1000\,\cancel{mL}}{1\,L} = \boxed{9.520\times10^{-2}\,M\ NaOH}$$

WA

Example 2: A 20.0 mL sample of 0.450 M HNO_2 is titrated with a 0.500 M NaOH solution. What volume of base is added at exactly halfway to the equivalence point?

↳of NaOH

- Draw a sketch of the set-up:



- What is the balanced reaction?

$$HNO_2 + NaOH \rightarrow H_2O + NaNO_2$$

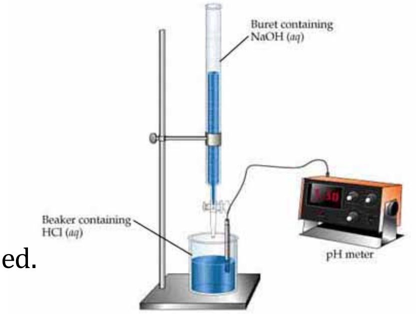
- What volume of NaOH was needed at equivalence point?

$$20.0\cancel{mL\ HNO_2} \times \frac{1\cancel{L}}{1000\cancel{mL}} \times \frac{0.450\cancel{mol\ HNO_2}}{1\cancel{L}} \times \frac{1\cancel{mol\ NaOH}}{1\cancel{mol\ HNO_2}} \times \frac{1L}{0.500\cancel{mol\ NaOH}}$$

$$= 0.0180\,L \text{ or } \boxed{18.0\,mL\ NaOH}$$

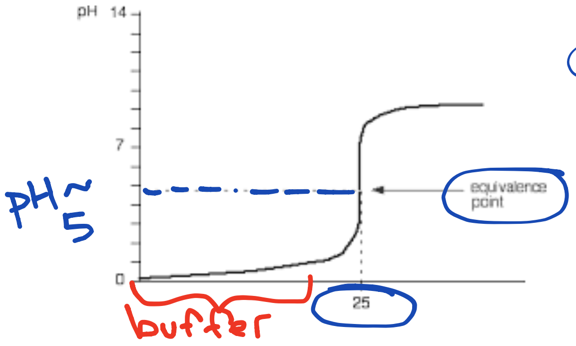
- What is halfway to equivalence point?

$$18.0\,mL \div 2 = \boxed{9.00\,mL\ NaOH}$$



TITRATION CURVES:

- A graph that plots the pH of the solution vs. the volume of the titrant added.



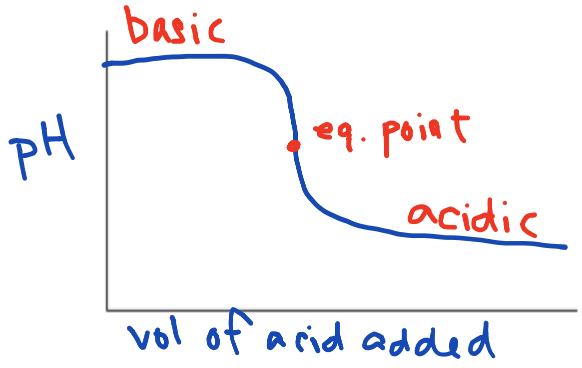
As the titrant is added, the pH is gradually (*[✓ increasing]*/*decreasing*) which means that (*acid*/*[✓ base]*) is the titrant.

How many mL of titrant was required to attain equivalence point? 25mL

Looking at the equivalence point pH, do you think the reaction produced [✓ an acidic] or basic salt?

pH < 7

What do you think the graph would look like if an acid was the titrant? Explain your answer.



pH would ↓ as acid is added

1. Strong Acid & Strong Base

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow \mathbf{NaCl_{(aq)}} + H_2O_{(l)}$

- Typical strong acid + strong base neutralization type of question.
  - (1) Dilution
  - (2) Neutralization
  - (3) Acidic or basic?

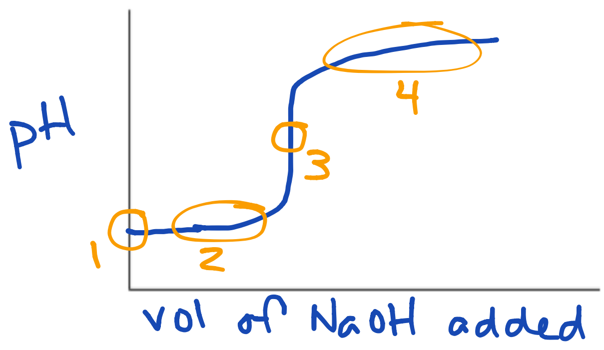
2. Weak Acid & Strong Base

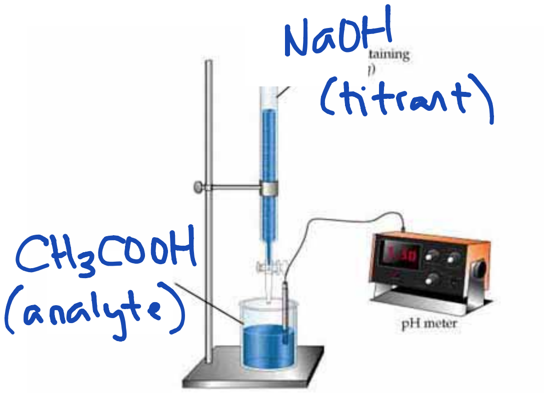
$$\overbrace{CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow \mathbf{NaCH_3COO_{(aq)}}}^{\text{buffer}} + H_2O_{(l)}$$

WA	SB	basic salt
50.0mL	?mL	
0.100M	0.150M	

50.0 mL of 0.100 M acetic acid is titrated with 0.150 M NaOH.

What do you think the pH curve will look like?





Because the pH meter is measuring **from the beaker**, we always have to think about <u>dilution</u>!

We will be calculating (and comparing) the pH at 4 points on the curve:

1. Before any titrant is added (weak acid)
2. Before reaching equivalence point (buffer)
3. At equivalence point (salt hydrolysis)
4. Beyond the equivalence point (strong base)

Calculate the pH of the solution produced in the reaction flask at the following points:

1) The pH of the solution of acetic acid when no NaOH is yet added.

- This is a weak acid calculation.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

I	0.100M		0	0
C	$-x$		$+x$	$+x$
E	0.100M $- x$		x	x

$$K_a = 1.8\times10^{-5} = \frac{x^2}{0.100-x}$$

assume $0.100 - x \cong 0.100$

$$x = 1.3\times10^{-3}\,M = [H_3O^+]$$

$$\boxed{pH = 2.87}$$

2) When 10.0 mL of 0.150 M NaOH has been added.

- Acts very similarly to a buffer as the added hydroxide ions reacts with acetic acid to produce acetate ions.
- What are the diluted concentrations of reactant acid and base before the reaction (initial concentrations)?

$[CH_3COOH]$

$$(0.100)(50.0) = C_2(60.0)$$

$$C_2 = 0.0833M = [CH_3COOH]$$

$[NaOH]$

$$(0.150)(10.0) = C_2(60.0)$$

$$C_2 = 0.0250M = [OH^-]$$

- Create an ICE table.

Spec Spec

	CH_3COOH +	$\cancel{Na}OH$ $\longrightarrow$	$\cancel{Na}CH_3COO$ +	H_2O
I	0.0833	0.0250	0	
C	−0.0250	−0.0250	+0.0250	
E	$\boxed{0.0583}$	0	$\boxed{0.0250}$	
	WA	buffer (acid)	WB	

- CH_3COOH and CH_3COO^- creates an acid buffer.

$$[H_3O^+] = K_a\left(\frac{[acid]}{[base]}\right)$$

$$= 1.8\times10^{-5}\left(\frac{0.0583}{0.0250}\right) = 4.2\times10^{-5}M$$

- Calculate the pH.

$$pH = -\log(4.2\times10^{-5})$$

$$= \boxed{4.38}$$

3) At the equivalence point when 33.3 mL of NaOH has been added.

33.3 mL NaOH @equiv. point

- What volume of NaOH is needed at equivalence point?

$CH_3COOH + NaOH \rightarrow NaCH_3COO + H_2O$

50.0 mL, 0.100M (CH₃COOH); ?mL, 0.150M (NaOH)

@equivalence point

$$50.0\,mL_{CH_3COOH} \times \frac{1L}{1000\,mL} \times \frac{0.100\,mol}{1L} \times \boxed{\frac{1\,mol_{NaOH}}{1\,mol_{CH_3COOH}}} \times \frac{1L}{0.150\,mol_{NaOH}} = 0.0333\,L$$

- What are the diluted concentrations of reactant acid and base before the reaction (initial concentrations)?

$[CH_3COOH]$

$(0.100)(50.0) = C_2(83.3)$

$C_2 = 0.0600M$

*should be equal!

$[NaOH]$

$(0.150)(33.3) = C_2(83.3)$

$C_2 = 0.0600M$

- Create an ICE table.

	CH_3COOH +	$NaOH$ →	$\cancel{Na}CH_3COO$ +	H_2O
I	0.0600	0.0600	0	
C	−0.0600	−0.0600	+0.0600	
E	0	0	0.0600	

- The anion of the dissociated salt, NaCH₃COO, is the conjugate base of a weak acid and is thus capable of accepting protons from water in a hydrolysis reaction.
- What is the hydrolysis reaction?

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

- Create an ICE table.

I	0.0600	0	0
C	$-x$	$+x$	$+x$
E	$0.0600-x$	x	x

- Calculate pH of the solution resulting from the anionic hydrolysis of the acetate ion.

$$K_b = \frac{K_w}{K_a(CH_3COOH)} = \frac{1.00\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = \frac{x^2}{0.0600-x}$$

*assume $0.0600-x \cong 0.0600$

$[OH^-] = x = 5.8\times10^{-6}M$

$pOH = 5.24$

$\boxed{pH = 8.76}$

4) **Beyond the equivalence point when 60.0 mL of NaOH added**

$[CH_3COOH]$

$(0.100)(50.0) = C_2\,(110.0)$

$C_2 = 0.0455M$

$[NaOH]$

$(0.150)(60.0) = C_2\,(110.0)$

$C_2 = 0.0818M$

$CH_3COOH + NaOH \rightarrow NaCH_3COO + H_2O$

I	0.0455	0.0818	0
C	-0.0455	-0.0455	+0.0455
E	0	0.0363	0.0455
		SB!	WB

$[OH^-] = 0.0363$

$pOH = 1.44$

$\boxed{pH = 12.56}$

Summary of Titrations

weak acid w/ strong base

HA = weak acid

CB = conjugate base

TB = titrant base (strong)

Scenario ① : No titrant added

*weak acid calculation

1. $HA + H_2O \rightleftharpoons CB + H_3O^+$ $\boxed{\text{ICE}}$
2. ICE w/ unknowns → use K_a → get $[H_3O^+]$ → pH

Scenario ② : Some titrant added (before equivalence point)

1. Find diluted [HA] and [TB]
2. $HA + \underset{\overset{\downarrow}{0}}{TB} \rightleftharpoons CB + H_2O$ $\boxed{\text{ICE}}$
3. Acid buffer : $HA + H_2O \rightleftharpoons CB + H_3O^+$
4. $[H_3O^+] = K_a\left(\frac{[HA]}{[CB]}\right) \longrightarrow pH$

Scenario ③ : At equivalence point

1. Find diluted [HA] and [TB]
2. $\underset{\overset{\downarrow}{0}}{HA} + \underset{\overset{\downarrow}{0}}{TB} \rightleftharpoons CB + H_2O$ $\boxed{\text{ICE}}$
3. [CB] hydrolysis : $CB + H_2O \rightleftharpoons HA + OH^-$ $\boxed{\text{ICE}}$
4. K_b from $[OH^-] \longrightarrow pOH \longrightarrow pH$

Scenario ④ : Beyond equivalence point

*strong base calculation

1. Find diluted [HA] and [TB]
2. $\underset{\overset{\downarrow}{0}}{HA} + TB \rightleftharpoons CB + H_2O$ $\boxed{\text{ICE}}$
3. $[TB] = [OH^-] \longrightarrow pOH \longrightarrow pH$

Practice:

WA SB

A 20.0 mL sample of 0.450 M HNO_2 is titrated with a 0.500 M NaOH solution. What will the pH be in the reaction flask at the following points:

a) 2.0 mL before exactly halfway to the equivalence point?

$$\underset{\substack{20.0\,mL \\ 0.450\,M}}{HNO_2} + \underset{\substack{?\,mL \\ 0.500\,M}}{NaOH} \longrightarrow NaNO_2 + H_2O$$

$$20.0\,mL_{HNO_2} \times \frac{1\,L}{1000\,mL} \times \frac{0.450\,mol_{HNO_2}}{1\,L} \times \frac{1\,mol\,NaOH}{1\,mol\,HNO_2} \times \frac{1\,L}{0.500\,mol} = 0.0180\,L$$

18.0 mL NaOH @equiv. point

$$(18.0\,mL \div 2) - 2.0\,mL = \boxed{7.0\,mL\,NaOH}$$

$[HNO_2]$

$$(0.450)(20.0) = C_2\,(27.0)$$

$$\boxed{[HNO_2] = 0.333\,M}$$

$[NaOH]$

$$(0.500)(7.0) = C_2(27.0)$$

$$\boxed{[NaOH] = 0.130\,M}$$

	HNO_2	+	spec. $\cancel{N}aOH$	$\rightleftharpoons$	spec. $\cancel{N}aNO_2$	+	H_2O
I	0.333M		0.130M		0		
C	-0.130M		-0.130M		+0.130M		
E	0.203M		0		0.130M		

acid buffer

$$[H_3O^+] = K_a\left(\frac{[HNO_2]}{[NO_2^-]}\right)$$

$$= 4.6\times10^{-4}\left(\frac{0.203}{0.130}\right)$$

$$= 7.2\times10^{-4}\,M$$

$$\boxed{pH = 3.14}$$

$\longrightarrow$ NaOH : 18.0mL

b) At equivalence point?

$[HNO_2]$

$(0.450)(20.0) = C_2(38.0)$

$[HNO_2] = 0.237M$

$[NaOH]$

$(0.500)(18.0) = C_2(38.0)$

$[NaOH] = 0.237M$

	HNO_2	+	$\cancel{Na}OH$	$\rightleftharpoons$	$\cancel{Na}NO_2$	+	H_2O
I	0.237M		0.237M		0		
C	-0.237M		-0.237M		+0.237M		
E	0		0		0.237M		

WB hydrolysis

	NO_2^-	+	H_2O	$\rightleftharpoons$	HNO_2	+	OH^-
I	0.237M				0		0
C	$-x$				$+x$		$+x$
E	$0.237-x$				x		x

$$K_b = \frac{K_w}{K_a(HNO_2)} = \frac{1.00\times10^{-14}}{4.6\times10^{-4}} = 2.2\times10^{-11} = \frac{x^2}{0.237}$$

*assume $0.237-x \cong 0.237$

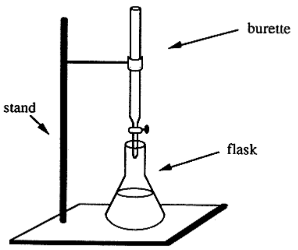
$$x = 2.3\times10^{-6}M = [OH^-]$$

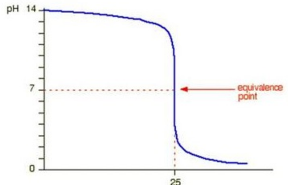
$$pOH = -\log(2.3\times10^{-6})$$
$$= 5.64$$

$$\boxed{pH = 8.36}$$

3. Strong Acid & Weak Base

$NH_3\,_{(aq)} + HCl\,_{(aq)} \rightarrow \mathbf{NH_4^+\,_{(aq)}} + Cl^-\,_{(aq)}$





100.0 mL of 0.050 M NH_3 is titrated with 0.10 M HCl.

Calculate the pH of the solution produced in the reaction flask at the following points:

1) Before any HCl is added.

pH = 10.98

2) At the midpoint of the titration.

pH = 9.25

3) At the equivalence point when _______ mL of HCl has been added.

pH = 5.37

4) When 60.0 mL of HCl has been added.

pH = 2.2

Practice:

Calculate the pH of the solution produced in the reaction flask when 13.00 mL of 0.100 M $HClO_4$ has been added to 25.00 mL of 0.100 M $NaNO_2$. (This is just beyond halfway to the equivalence point.)

pH = 3.30

Indicators

We measure pH using either an acid-base indicator or a pH meter. Acid-base indicators are weak organic acids whose conjugate pairs display different and normally intense colours.

Acid-base indicators are complex organic molecules and refer to them as simply "HIn."

$$\underline{HIn} + H_2O \leftrightharpoons \underline{In^-} + H_3O^+$$

Acidic Form
Displays a unique colour when $[H_3O^+]$ is high

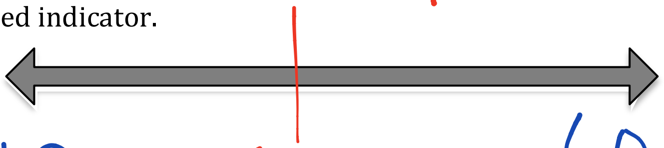
Basic Form
Displays a unique colour when $[H_3O^+]$ is low

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

ratio!

- transition point
- equivalence point

Example: Consider methyl red indicator.



pH: 4.8 5.4 6.0

Colour: red orange yellow

- The pH value at which the indicator exhibits a colour change should be close to the pH at equivalence point. (red → orange ← yellow).
- When the colour changes, (reached transition point) it is an indication that the titration has reached equivalence point. At this point, $K_a = [H_3O^+]$ b/c $[HIn] = [In^-]$

pH at equivalence point	$[H_3O^+]$	Indicator	Colour exhibited
11.05	8.9×10^{-12} M	Alizarin yellow	orange
6.8	1.6×10^{-7} M	Bromothymol Blue	green
9.1	7.9×10^{-10} M	phenolphthalein	Light pink
8.8	1.6×10^{-9} M	Thymol blue	Green
2.0	1.0×10^{-2} M	Thymol blue	Orange

*Looking for equivalence point! (Scenario 3)

When 1.0 M NH_3 is titrated with 1.0 M HCl, the most suitable indicator is:

when volume is doubled, [ ] is halved

A. methyl violet.
B. indigo carmine.
C. phenolphthalein.
[✓ D. bromcresol green.]

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

	NH_3	HCl	NH_4^+
I	0.50M	0.50M	0
C	-0.50M	-0.50	+0.50
E	0	0	0.50

hydrolyzes (WA)

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

	NH_4^+	NH_3	H_3O^+
I	0.50	0	0
C	$-x$	$+x$	$+x$
E	$0.50-x$	x	x

*assume $0.50 - x \cong 0.50$

$K_a = 5.6\times10^{-10} = \frac{x^2}{0.50-x}$

$x = \sqrt{(5.6\times10^{-10})(0.50)}$

$[H_3O^+] = 1.7\times10^{-5}$ M

pH = 4.78 → transition point pH

The most appropriate indicator for the titration of 0.50 M CH_3COOH with 0.50 M NaOH is

A. methyl violet.
B. indigo carmine.
[✓ C. phenolphthalein.]
D. bromcresol green.

$CH_3COOH + NaOH \rightarrow NaCH_3COO^- + H_2O$

	CH_3COOH	NaOH	$NaCH_3COO^-$
I	0.25M	0.25M	0
C	-0.25	-0.25	+0.25
E	0	0	0.25

hydrolyzes (WB)

$K_b = \frac{K_w}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$\cancel{Na}CH_3COO + H_2O \rightleftharpoons CH_3COOH + \cancel{Na}OH$

	CH_3COO	CH_3COOH	OH
I	0.25M	0	0
C	$-x$	$+x$	$+x$
E	$0.25-x$	x	x

↳ assume $0.25-x \cong 0.25$

$5.6\times10^{-10} = \frac{x^2}{0.25}$

$x = \sqrt{(5.6\times10^{-10})(0.25)}$

$x = 1.2\times10^{-5}$ M $= [OH^-]$

pOH = 4.93

pH = 9.07

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