

Sections 10.7 and 10.8 غير مطلوبة

Chapter 10: Acid-Base Titrations

- Titrations are Important tools in providing quantitative and qualitative data for a sample.
- To best understand titrations and the information they provide, it is necessary to understand what gives rise to the shape of a typical titration curve.
- To do this, acid-base equilibria are used to predict titration curve shapes.

10.1 Titration of Strong Acid with Strong Base

1.) Titration curve is a graph shows of how pH changes as titrant is added

- Assume strong acid and base completely dissociate
- *Any amount of H^+ added will consume a stoichiometric amount of OH^-*

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Because the equilibrium constant for this reaction is 10^{14} , it is fair to say that it “goes to completion

- Three regions of the titration curve
 - **Before the equivalence point, the pH is determined by excess OH^- in the solution**
 - **At the equivalence point, H^+ is just sufficient to react with all OH^- to make H_2O**
 - **After the equivalence point, pH is determined by excess H^+ in the solution.**

- Remember, equivalence point is the ideal goal
- Actually measure End Point
 - **Marked by a sudden physical change: color, potential**
- Different Regions require different kinds of calculations
 - **Illustrated examples**
- The “true” titration reaction is:



2.) Volume Needed to Reach the Equivalence Point

- **Titration curve for 50.00 mL of 0.02000 M KOH with 0.1000 M HBr**
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- At equivalence point, amount of H^+ added will equal initial amount of OH^-

$$(V_e \text{ (mL)}) (0.1000 \text{ M}) = (50.00 \text{ mL}) (0.02000 \text{ M}) \Rightarrow V_e = 10.00 \text{ mL}$$

mmol of HBr mmol of OH^-
at equivalence point being titrated

*When 10.00 mL of HBr has been added, the titration is complete.
Prior to this point, there is excess OH^- present.
After this point there is excess H^+ present.*

3.) Before the Equivalence Point

- Before adding HBr: $\text{pOH} = -\log 0.02000 = 1.70$
 $\text{pH} = 14.00 - 1.70 = 12.30$
- Equivalence point (V_e) when 10.00 mL of HBr has been added

- **When 3.00 mL of HBr has been added, reaction is 3/10 complete**

$$\text{mmoles KOH present} = 0.02000 \text{ mmol/mL} \times 50.00 \text{ mL} = 1.000$$

$$\text{mmoles HBr added} = 0.1000 \text{ mmol/mL} \times 3.00 \text{ mL} = 0.300$$

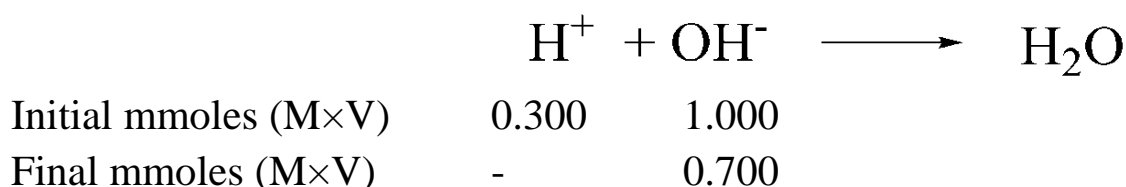
$$\text{mmoles KOH remain} = 1.000 - 0.300 = 0.700$$

$$[\text{KOH}] \text{ remain} = 0.700 \text{ mmol}/53.00 \text{ mL} = 0.0132 \text{ M} = [\text{OH}^-]$$

Calculate $[\text{H}^+]$ and pH

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0132} = 7.58 \times 10^{-13} \text{ M} \Rightarrow \text{pH} = 12.12$$

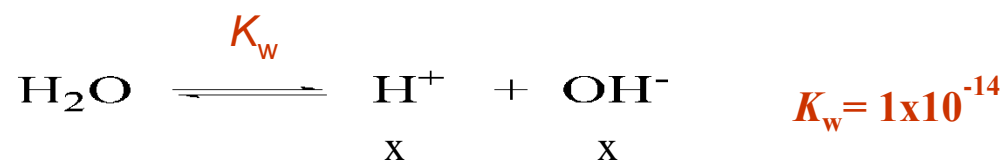
Or



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4.) **At the Equivalence Point**

- **Just enough H^+ has been added to consume OH^-**
- **pH determined by dissociation of water**



$$K_w = x^2 \Rightarrow x = 1.00 \times 10^{-7} \text{ M} \Rightarrow \text{pH} = 7.00$$

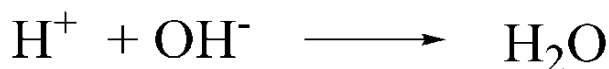
- ***pH at the equivalence point for any strong acid with strong base is 7.00***
- **Not true for weak acid-base titration**

5.) **After the Equivalence Point**

- **Adding excess HBr solution**
- **When 10.50 mL of HBr is added**

- mmoles KOH present = $0.02000 \text{ mmol/mL} \times 50.00 \text{ mL} = 1.000$
- mmoles HBr added = $0.1000 \text{ mmol/mL} \times 10.50 \text{ mL} = 1.050$
- mmoles HBr remain = $1.050 - 1.000 = 0.050$
- $[\text{HBr}]_{\text{remain}} = 0.050 \text{ mmol}/60.5 \text{ mL} = 8.26 \times 10^{-4} \text{ M} = [\text{H}^+]$

$$\text{pH} = -\log[\text{H}^+] = -\log(8.26 \times 10^{-4} \text{ M}) = 3.08$$



Initial mmoles (M×V)	1.050	1.000
Final mmoles (M×V)	0.050	-

- Rapid Change in pH Near Equivalence Point

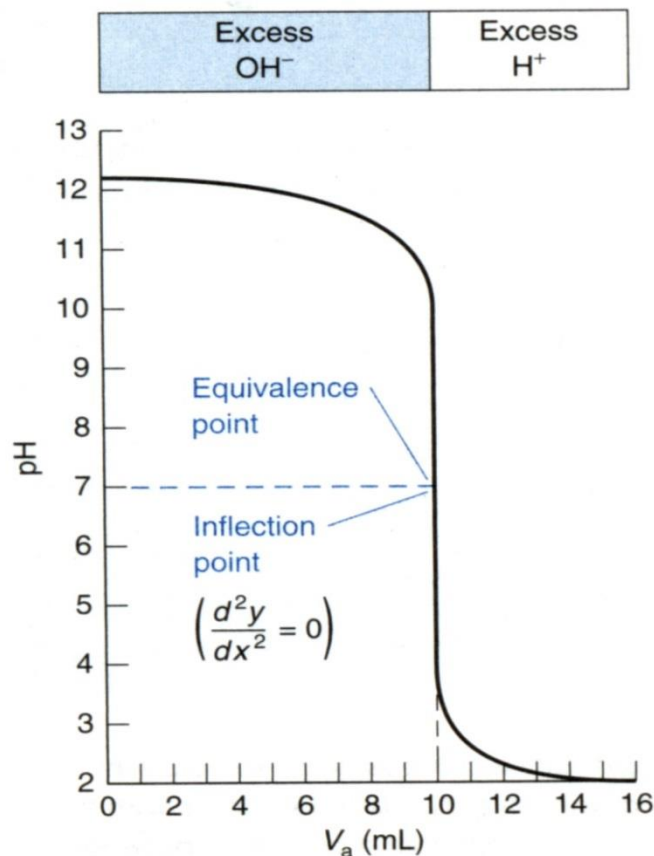
- **Equivalence point is where slope is greatest**
- **Second derivative is 0**

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All Titration Curves have a characteristic

“Sigmoid (S-shaped) profile

- *Beginning of Curve: pH changes slowly
- *Middle of Curve: pH changes very rapidly
- *End of Curve: pH changes very slowly again

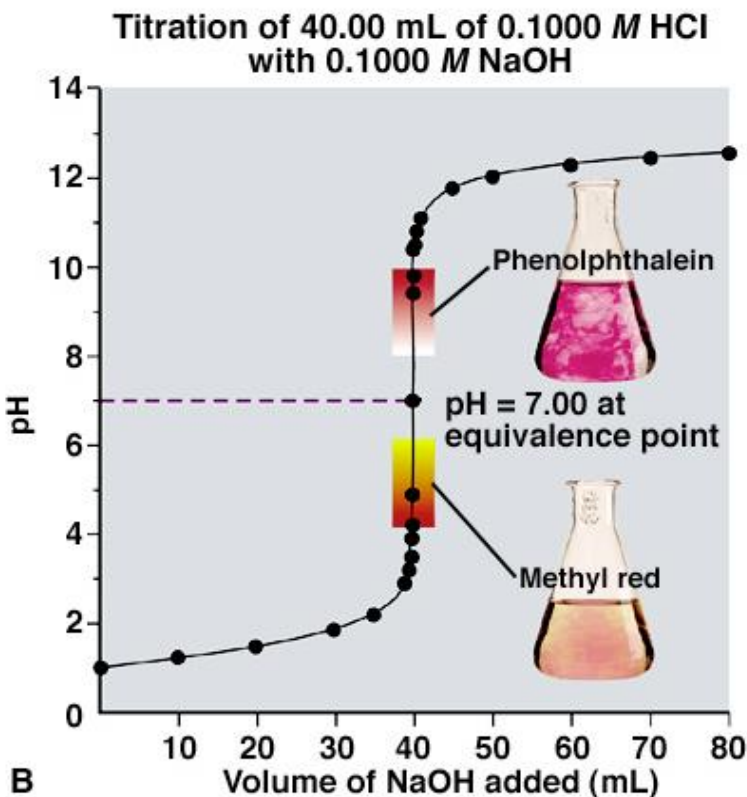


Strong Acid-Base Titration Curve

Volume of NaOH added (mL) pH

00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A



B

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- The previous curve shows how the pH of the solution changes during the titration of 40.0 mL of 0.100 M HCl, a strong acid with 0.100 M NaOH, a strong base.
- The initial pH of the 0.100 M HCl is 1.00.
 - As NaOH is added, the acid is neutralized and the solution's pH increases gradually.
 - When nearly all of the H^+ ions from the acid have been used up, the pH increases dramatically with the addition of an exceedingly small volume of NaOH.
 - This abrupt change in pH occurs at the equivalence point of the titration.
 - Beyond the equivalence point, the addition of more NaOH again results in the gradual increase in pH.

10.2 Titration of Weak Acid with Strong Base

1.) Four Regions to Titration Curve

➤ Before any added base, just weak acid (HA) in water

- pH determined by K_a



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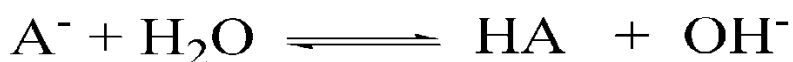
➤ With addition of strong base → buffer

- pH determined by Henderson Hasselbach equation

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

➤ At equivalence point, all HA is converted into A^-

- Weak base with pH determined by K_b



➤ Beyond equivalence point, excess strong base is added to A^- solution

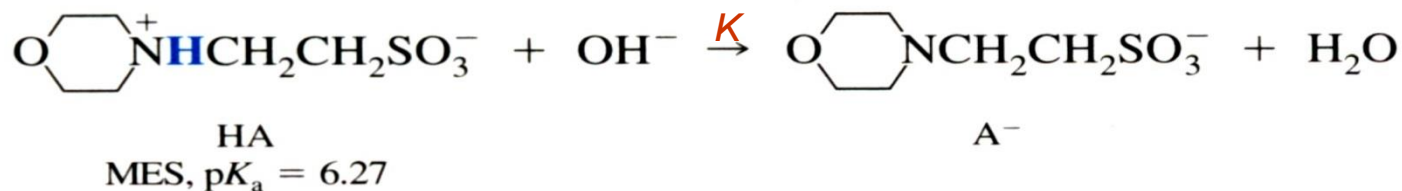
- pH is determined by strong base

- Similar to titration of strong acid with strong base

2.) Illustrated Example:

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

- MES is a weak acid with $pK_a = 6.27$



- Reaction goes to completion with addition of strong base

$$K = \frac{1}{K_b} = \frac{1}{(K_w / K_a)} = \frac{1}{(1 \times 10^{-14} / 10^{-6.27})} = 5.4 \times 10^7$$

3.) Volume Needed to Reach the Equivalence Point

➤ Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

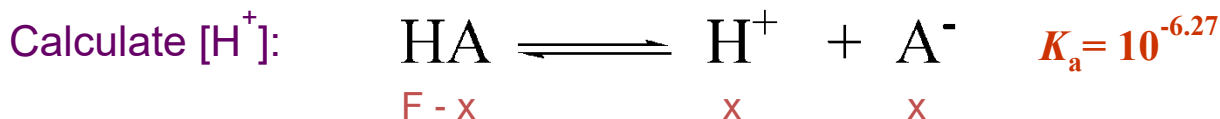
- Reaction goes to completion with addition of strong base
- **Strong plus weak react completely**

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$$\underbrace{(V_e \text{ (mL)})}_{\text{mmol of KOH}} \underbrace{(0.1000 \text{ M})}_{\text{mmol of KOH}} = \underbrace{(50.00 \text{ mL})}_{\text{mmol of MES}} \underbrace{(0.02000 \text{ M})}_{\text{mmol of MES}} \Rightarrow V_e = 10.00 \text{ mL}$$

4.) Region 1: Before Base is Added

➤ Simply a weak-acid problem



$$\frac{x^2}{F - x} = \frac{x^2}{0.02000 - x} = K_a \Rightarrow x = [H^+] = 1.03 \times 10^{-4}$$

Calculate pH:

$$pH = -\log[H^+] = -\log(1.03 \times 10^{-4} \text{ M}) = 3.99$$

5.) Region 2: Before the Equivalence Point

- Adding OH^- creates a mixture of HA and $\text{A}^- \rightarrow \text{Buffer}$
- Calculate pH from $[\text{A}^-]/[\text{HA}]$ using Henderson-Hasselbach equation

Calculate $[\text{A}^-]/[\text{HA}]$:

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- Amount of added NaOH is 3 mL with equivalence point is 10 mL

	$\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$	
Initial mmoles	1.000	0.300
Final mmoles	0.700	-
		0.300

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = 6.27 + \log\left(\frac{3/10}{7/10}\right) = 5.90$$

- $\text{pH} = \text{pK}_a$ when the volume of titrant equals $1/2 V_e$

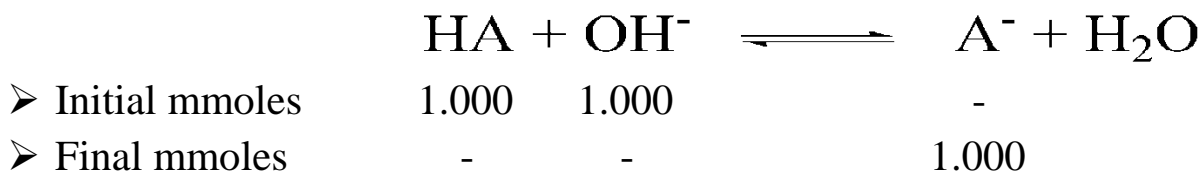
	$\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$	
Initial mmoles	1.000	0.500
Final mmoles	0.500	-
		0.500

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \text{pK}_a + \log\left(\frac{1/2}{1/2}\right) = \text{pK}_a$$

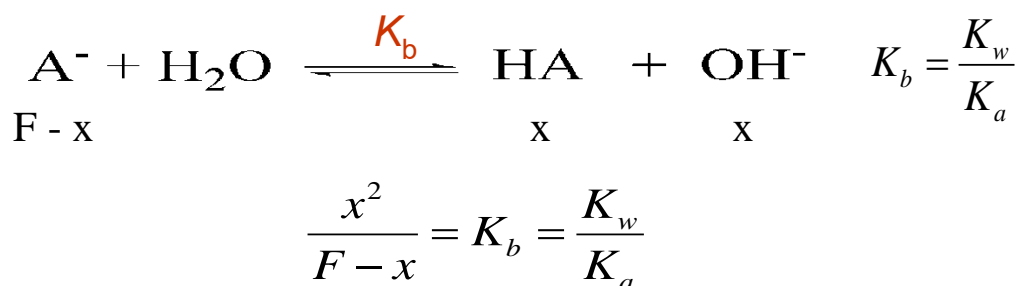
pH at midpoint of “Buffer” region is common method of estimating pK_a of an “unknown” acid

5.) Region 3: At the Equivalence Point

Exactly enough NaOH to consume HA



➤ The solution only contains $\text{A}^- \rightarrow$ weak base



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Calculate Formal concentration of $[\text{A}^-]$:

A^- is no longer 0.02000 M, diluted by the addition of NaOH

$$M_i \times V_i = M_f \times V_f \rightarrow 50.00 \times 0.02000 = M_f \times 60.00 \rightarrow M_f = 0.0167M$$

Calculate $[\text{OH}^-]$:

$$\frac{x^2}{F - x} = K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-6.27}} = 1.86 \times 10^{-8}$$

$$\frac{x^2}{0.0167 - x} = 1.86 \times 10^{-8} \Rightarrow x = [\text{OH}^-] = 1.76 \times 10^{-5} M$$

Calculate pH:

$$\text{pOH}^- = -\log 1.76 \times 10^{-5} = 4.75 \quad \text{and} \quad \text{pH} = 14.00 - 4.75 = 9.25$$

pH will always be **above** 7.00 for titration of a weak acid because acid is converted into conjugate base at the equivalence point

5.) Region 4: After the Equivalence Point

Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

➤ Adding NaOH to a solution of A⁻

- **NaOH is a much stronger base than A⁻**

- **pH determined by excess of OH⁻**

Calculate [OH⁻]:

Amount of added NaOH is 10.10 mL with equivalence point is 10 mL

	$\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$	
Initial mmoles	1.000	1.010
Final mmoles	-	0.010
		1.00

$$[\text{OH}^-]_{\text{excess}} = \frac{0.010 \text{ mmol}}{60.10} = 1.66 \times 10^{-4}$$

$$\text{pOH} = -\log 1.66 \times 10^{-4} = 3.78$$

$$\text{pH} = 14.00 - 3.78 = 10.22$$

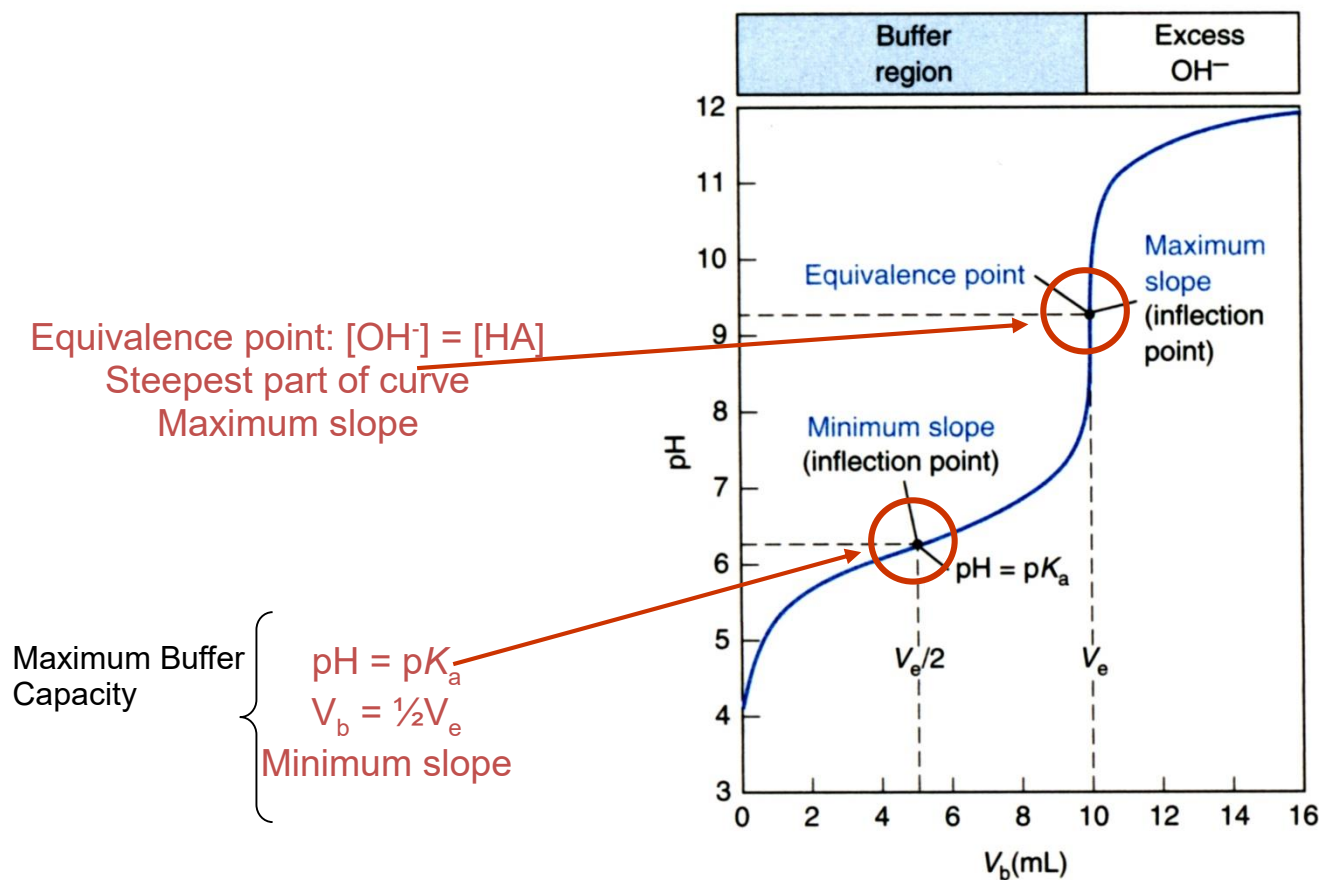
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5.) Titration Curve

➤ Titration of 50.00 mL of 0.02000 M MES with 0.1000 M NaOH

➤ *Two Important Features of the Titration Curve*

➤ *The gradually arising portion of the curve before the steep rise to the equivalence point is called the “buffer region”*



Titration Curve

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- Depends on pK_a or acid strength
- Inflection point or maximum slope decreases with weaker acid
 - *Equivalence point becomes more difficult to identify*

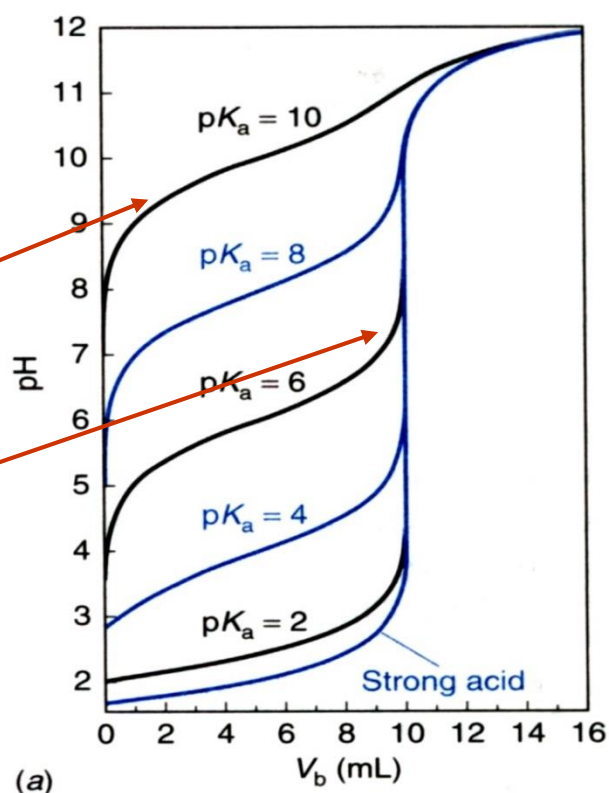
weak acid → small slope change in titration curve

Difficult to detect equivalence point

Strong acid → large slope change in titration curve

Easy to detect equivalence point

- Depends on acid concentration



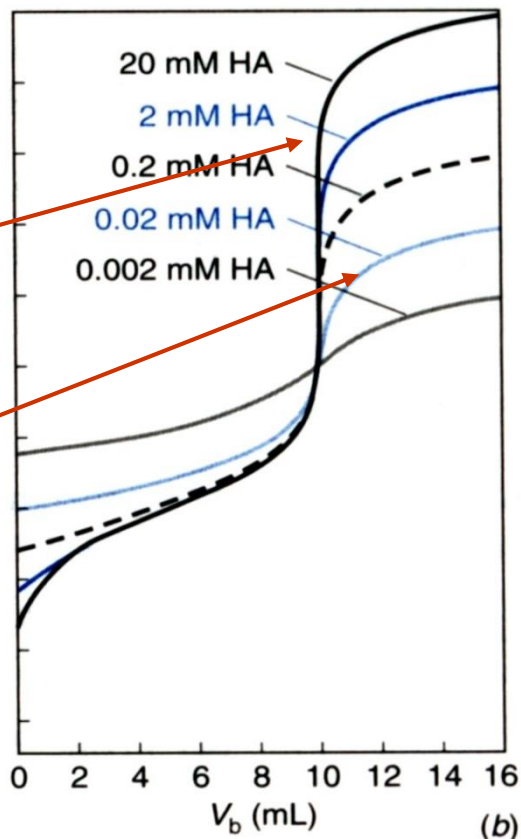
- Inflection point or maximum slope decreases with lower acid concentration
 - **Equivalence point becomes more difficult to identify**
 - **Eventually can not titrate acid at very low concentrations**

High concentration → large slope change
in titration curve
Easy to detect equivalence point

Low concentration → small slope change
in titration curve
Difficult to detect equivalence point

At low enough concentration, **can not detect change in titration curve**

Difficult to detect equivalence point



As the acid becomes weaker or more dilute, the end point becomes less distinct.

10.3 Titration of Weak Base with Strong Acid

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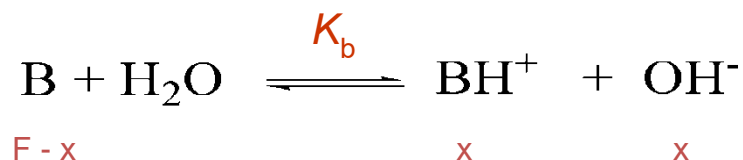
1.) Simply the Reverse of the Titration of a Weak Acid with a Strong Base

- **Again, Titration Reaction Goes to Completion:**



- **Again, Four Distinct Regions to Titration Curve**
- **Before acid is added → just weak base reaction**

- pH determined from K_b



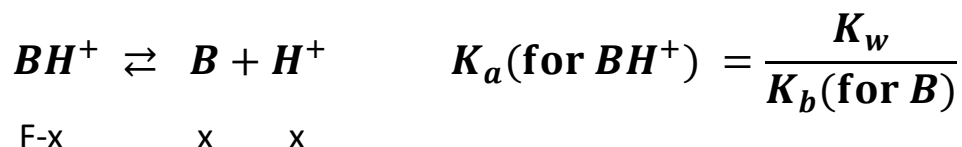
➤ Before equivalence point, → *buffer*

- pH determined from Henderson Hasselbach equation

$$pH = pK_a(\text{for } BH^+) + \log \frac{[BH^+]}{[B]}$$

- $V_a = \frac{1}{2}V_e$ then $pH = pK_a$ (for BH^+)
- pK_a and pK_b can be determined from titration curves

➤ At the equivalence point, B has been converted into BH^+ , a weak acid. The pH is calculated by considering the acid dissociation reaction of BH^+ .



The formal concentration of BH^+ , F, is not the original formal concentration of B because some dilution has occurred. The solution contains BH^+ at the equivalence point, so it is acidic. *The pH at the equivalence point must be below 7.*

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➤ After the equivalence point, the excess strong acid determines the pH. We neglect the contribution of weak acid, BH^+ .

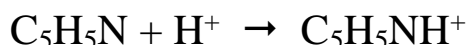
EXAMPLE Titration of Pyridine with HCl

Consider the titration of 25.00 mL of 0.083 64 M pyridine with 0.106 7 M HCl.
 K_b for pyridine (C_5H_5N) = 1.59×10^{-9}

$$K_a(C_5H_5NH^+) = \frac{K_w}{K_b} = 6.31 \times 10^{-6} \rightarrow pK_a = 5.20$$

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The titration reaction is:



and the equivalence point occurs at 19.60 mL:

$$\text{mmol HCl} = \text{mmol pyridine}$$

$$(0.1067 M)(V_e \text{ mL}) = (0.08364 M \times 25.00 \text{ mL}) \rightarrow V_e = 19.60 \text{ mL}$$

Before the equivalence point:

Find the pH when $V_a = 4.63$ mL (after adding 4.63 mL of HCl solution).

Solution Part of the pyridine has been neutralized, so there is a mixture of pyridine and pyridinium ion (*A buffer*)

$$\text{mmol } C_5H_5N = (0.08364 M \times 25.00 \text{ mL}) - (0.1067 M)(4.63 \text{ mL}) = 1.60$$

$$\text{mmol } C_5H_5NH^+ = \text{mmol HCl added} = (0.1067 M)(4.63 \text{ mL}) = 0.494$$

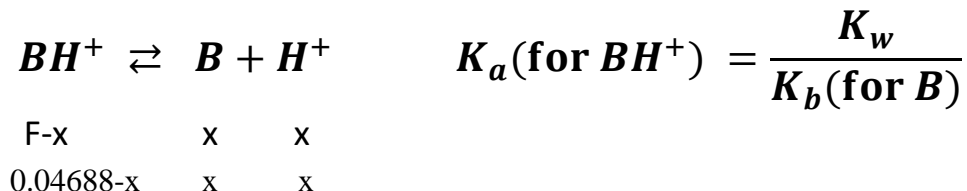
$$pH = pK_a + \log \frac{[C_5H_5N]}{[C_5H_5NH^+]} = 5.20 + \log \frac{1.60 \text{ mmol}}{0.494 \text{ mmol}} = 5.71$$

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 29.63 مل.

Test Yourself Find the pH when $V_a = 14.63$ mL. (Answer: 4.73)

At the equivalence point:

Test Yourself Find the pH when $V_a = 19.60$ mL. (Answer: 3.2645)



$$K_a(C_5H_5NH^+) = \frac{K_w}{K_b} = 6.31 \times 10^{-6}$$

$$x = [H^+] = 5.439 \times 10^{-4} \rightarrow pH = 3.2645$$

After the equivalence point:

Test Yourself Find the pH when $V_a = 20.60$ mL. (Answer: 2.6296)

$$[H^+] = \frac{0.1070 \text{ mmol}}{45.60 \text{ mL}} = 2.3465 \times 10^{-3} M \rightarrow pH = 2.6296$$

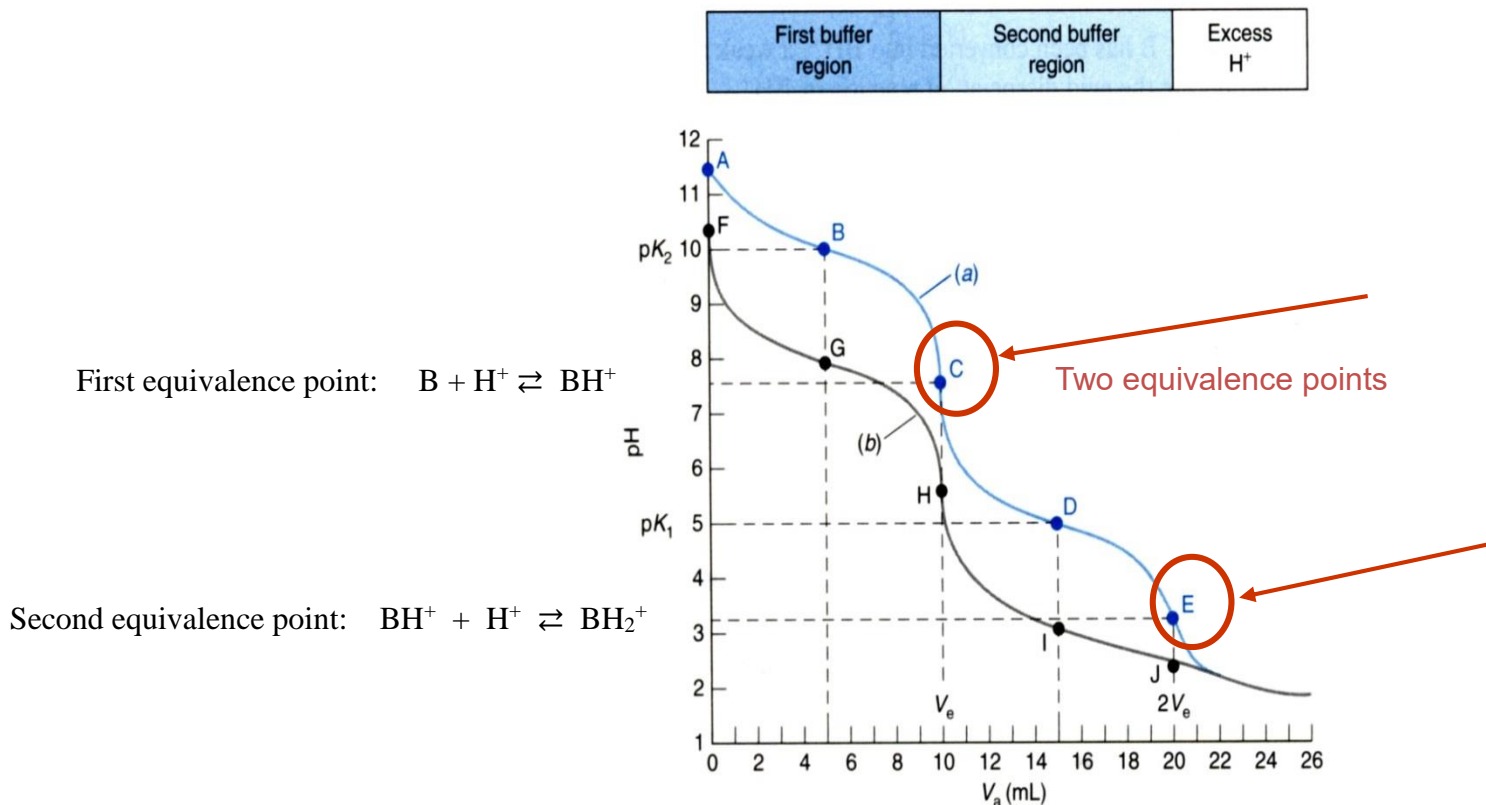
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10.4 Titration in Diprotic Systems

1.) Principles for Monoprotic Systems Apply to Diprotic Systems

- Multiple equivalence points and buffer regions
- Multiple Inflection Points in Titration Curve

FIGURE 10-4 (a) Titration of 10.0 mL of 0.100 M base ($pK_{b1} = 4.00$, $pK_{b2} = 9.00$) with 0.100 M HCl. The two equivalence points are C and E. Points B and D are the half-neutralization points, whose pH values equal pK_{a2} and pK_{a1} , respectively. (b) Titration of 10.0 mL of 0.100 M nicotine ($pK_{b1} = 6.15$, $pK_{b2} = 10.85$) with 0.100 M HCl. There is no sharp break at the second equivalence point, J, because the pH is too low.



2.) A Typical Case

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Titration of 10.0 mL of 0.100 M base (B) with 0.100 M HCl

- $pK_{b1} = 4.00$ and $pK_{b2} = 9.00$

➤ Volume at First Equivalence Point (V_e)

$$\underbrace{(V_e \text{ (mL)})}_{\text{mmol of HCl}} \underbrace{(0.100 \text{ M})}_{\text{mmol of B}} = \underbrace{(10.00 \text{ mL})}_{\text{mmol of B}} \underbrace{(0.1000 \text{ M})}_{\text{mmol of HCl}} \Rightarrow V_e = 10.00 \text{ mL}$$

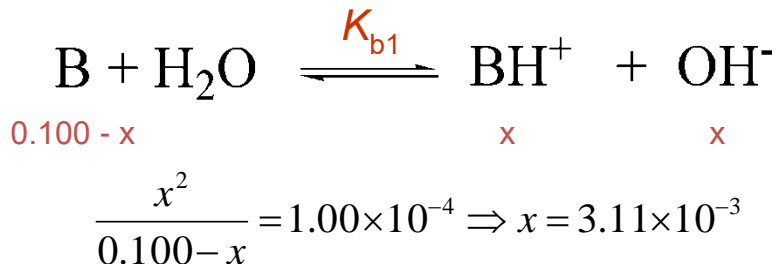
➤ Volume at Second Equivalence Point **Must Be** $2V_e$

- Second reaction requires the same number of moles of HCl

2.) A Typical Case

➤ Point A

- **Before Acid Added**
- **Weak base problem**



$$[H^+] = \frac{K_w}{x} \Rightarrow pH = 11.49$$

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➤ Point between A & B

- **Before First Equivalence Point**
- **Buffer problem**

➤ **Remember:** $K_{b1} \times K_{a2} = K_w$ *and* $K_{b2} \times K_{a1} = K_w$

Point (1.5 mL) is before first equivalence point (10 mL)

	B	+	H ⁺	⇌	BH ⁺
Initial mmoles	1.00		0.15		0
Final mmoles	0.85		0		0.15

$$K_{a2} = \frac{K_w}{K_{b1}} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}$$

$$pH = pK_a + \log \frac{[B]}{[BH^+]} = 10.00 + \log \frac{0.85}{0.15} = 10.75$$

Point B (5 mL) is halfway to first equivalence point (10 mL)

	$B + H^+ \rightleftharpoons BH^+$		
Initial mmoles	1.00	0.50	0
Final mmoles	0.50	0	0.50

$$pH = pK_{a2} + \log \frac{[B]}{[BH^+]} = 10.00 + \log \frac{0.50}{0.50} = 10.00$$

$$pH = pK_{a2} = 10.00$$

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➤ Point C

- First Equivalence Point

At the first equivalence point, B has been converted into BH^+ , the intermediate form of the diprotic acid, BH_2^+ . BH^+ is both an acid and a base. From Equation 9-11, we know that

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}} \quad (9-11)$$

	$B + H^+ \rightleftharpoons BH^+$		
Initial mmoles	1.00	1.00	0
Final mmoles	0.00	0.00	1.00

Account for dilution for formal concentration (F) of BH^+
 $[BH^+] = 1.00 \text{ mmol} / 20.00 \text{ mL} = 0.0500 \text{ M}$

$$K_{a2} = \frac{K_w}{K_{b1}} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10} \quad K_{a1} = \frac{K_w}{K_{b2}} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5}$$

$$[H^+] = \sqrt{\frac{(10^{-10})(10^{-5})(0.0500) + (10^{-5})(10^{-14})}{(10^{-5}) + (0.0500)}} = 3.17 \times 10^{-8} \text{ M}$$

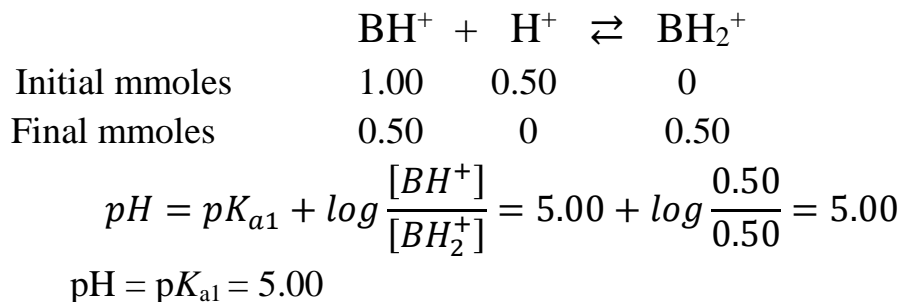
$$pH = -\log 3.17 \times 10^{-8} = 7.50$$

$$\text{Note that, in this example, } pH \approx \frac{1}{2}(pK_1 + pK_2) \quad (9.12)$$

➤ Point D

- At any point between C and E, there is a buffer containing BH^+ (the base) and BH_2^+ (the acid).

Point D (15 mL) is halfway to second equivalence point (2x10 mL).



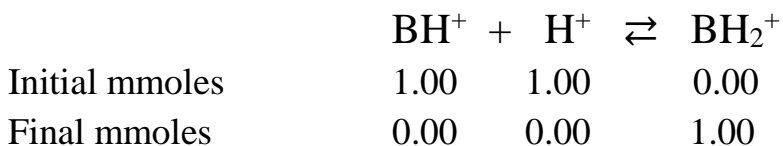
Calculate pH after adding 17.2 mL of 0.100 M HCl

Answer: 4.59

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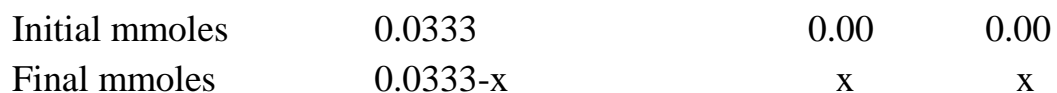
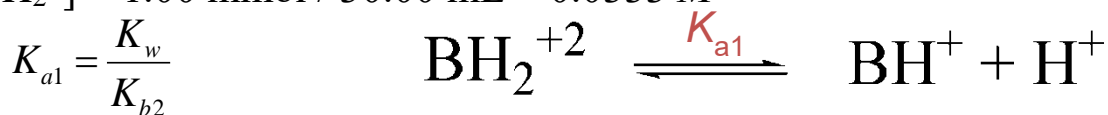
➤ Point E

- **Second Equivalence Point**
- **Weak acid problem**



Account for dilution for formal concentration (F) of BH_2^+

$$[BH_2^+] = 1.00 \text{ mmol} / 30.00 \text{ mL} = 0.0333 \text{ M}$$



$$\frac{x^2}{F-x} = \frac{x^2}{0.0333-x} = 1.0 \times 10^{-5}$$

$$\Rightarrow x = 5.72 \times 10^{-4} \Rightarrow pH = 3.24$$

- Beyond Point E
 - **Past Second Equivalence Point**
 - **Strong acid problem**

pH from volume of strong acid added. Addition of 25.00 mL:

Excess acid:

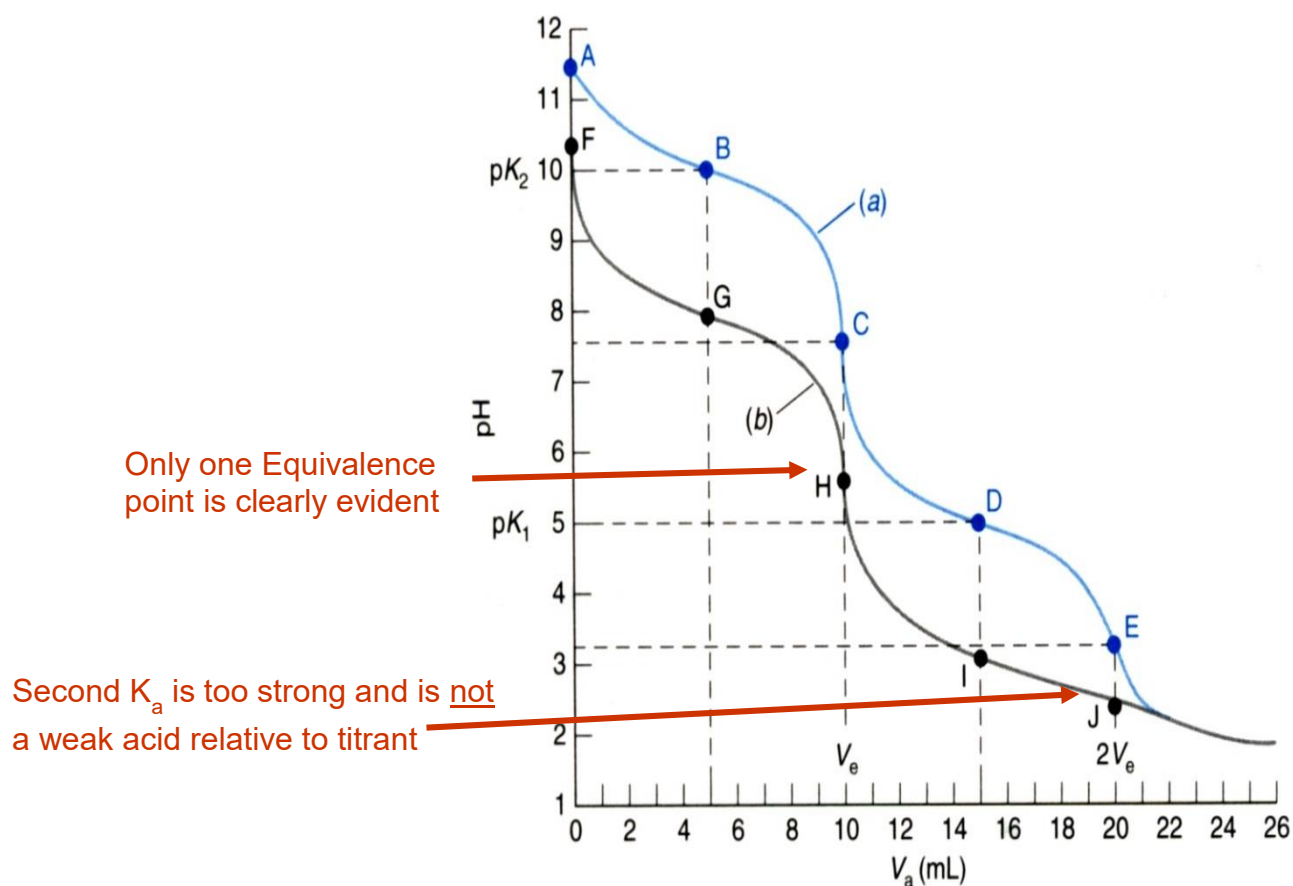
$$V_{added} - V_{equivalence} = 25.00 - 20.00 = 5.00 \text{ mL}$$

Concentration of H^+ :

$$[H^+]_{excess} = \frac{(0.100 \text{ mmol/mL})(5.00 \text{ mL})}{(25.00 + 5.00) \text{ mL}} = 1.43 \times 10^{-2} M$$

$$\text{pH} = -\log[H^+] = -\log(1.43 \times 10^{-2}) = 1.85$$

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(a) Titration of 10.0 mL of 0.100 M base ($pK_{b1} = 4.00$, $pK_{b2} = 9.00$) with 0.100 M HCl. The two equivalence points are C and E. Points B and D are the half- neutralization points, whose pH values equal pK_{a2} and pK_{a1} , respectively. (b) Titration of 10.0 mL of 0.100 M nicotine ($pK_{b1} = 6.15$, $pK_{b2} = 10.85$) with 0.100 M HCl. There is no sharp break at the second equivalence point, J, because the pH is too low.

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Blurred End Points

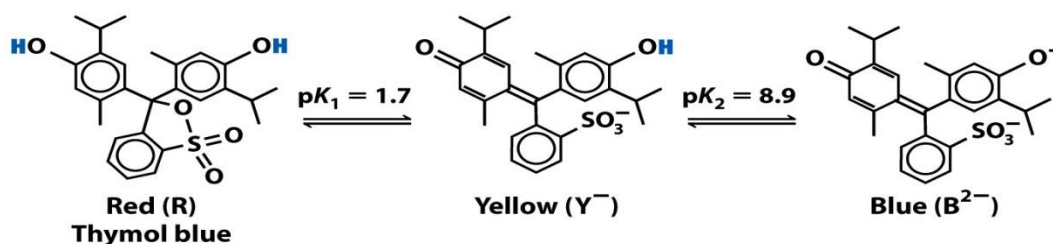
Titration of many diprotic acids or bases show two clear end points, as in curve a in Figure 10-4. Some titrations do not show both end points, as illustrated by curve b, which is calculated for the titration of 10.0 mL of 0.100 M nicotine ($pK_{b1} = 6.15$, $pK_{a2} = 10.85$) with 0.100 M HCl.

There is no perceptible break at the second equivalence point (J), because BH_2^+ is too strong an acid (or, equivalently, BH^+ is too weak a base).

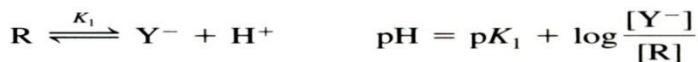
10.6 Finding the end point with indicators

Indicators: compounds added in an acid-base titration to allow end point detection

- Common indicators are weak acids or bases
- Different protonated species have different colors, an example is thymol blue.



Unnumbered figure pg 213a
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pH	$[Y^-]:[R]$	Color
0.7	1:10	red
1.7	1:1	orange
2.7	10:1	yellow

2.) Choosing an Indicator

- Want Indicator that changes color in the vicinity of the equivalence point and corresponding pH
- The closer the two match, the more accurate determining the end point will be

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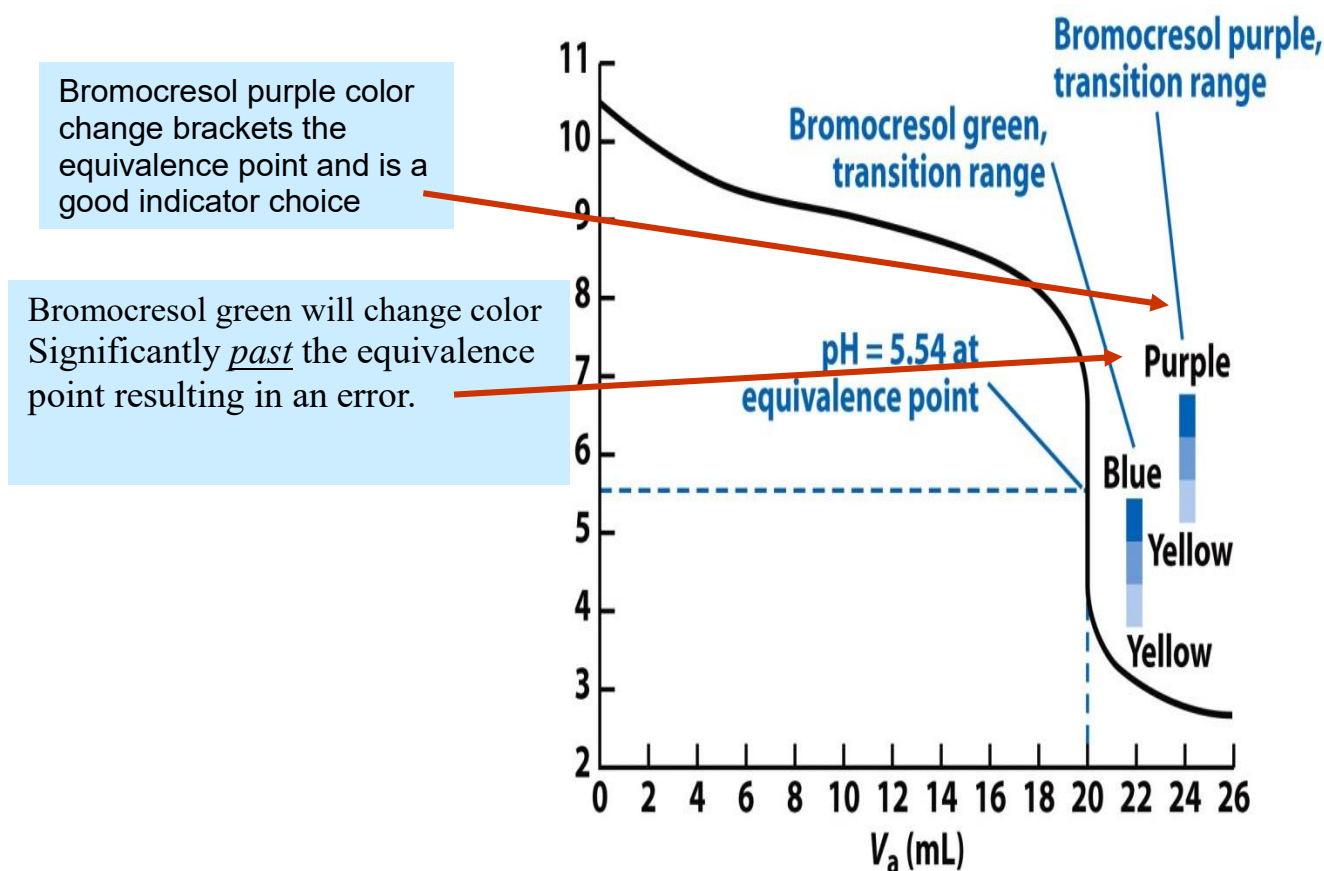


Figure 11-9
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The above figure is a calculated titration curve for the reaction of 100 mL of 0.010 0 M base ($\text{p}K_b = 5.00$) with 0.050 0 M HCl.

Table 11-4 Common Indicators

Indicator	Transition range (pH)	Acid color	Base color	Preparation
Methyl violet	0.0–1.6	Yellow	Violet	0.05 wt% in H ₂ O
Cresol red	0.2–1.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Thymol blue	1.2–2.8	Red	Yellow	0.1 g in 21.5 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Cresol purple	1.2–2.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Erythrosine, disodium	2.2–3.6	Orange	Red	0.1 wt% in H ₂ O
Methyl orange	3.1–4.4	Red	Yellow	0.01 wt% in H ₂ O
Congo red	3.0–5.0	Violet	Red	0.1 wt% in H ₂ O
Ethyl orange	3.4–4.8	Red	Yellow	0.1 wt% in H ₂ O
Bromocresol green	3.8–5.4	Yellow	Blue	0.1 g in 14.3 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Methyl red	4.8–6.0	Red	Yellow	0.02 g in 60 mL ethanol. Then add 40 mL H ₂ O.
Chlorophenol red	4.8–6.4	Yellow	Red	0.1 g in 23.6 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Bromocresol purple	5.2–6.8	Yellow	Purple	0.1 g in 18.5 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
p-Nitrophenol	5.6–7.6	Colorless	Yellow	0.1 wt% in H ₂ O
Litmus	5.0–8.0	Red	Blue	0.1 wt% in H ₂ O
Bromothymol blue	6.0–7.6	Yellow	Blue	0.1 g in 16.0 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Phenol red	6.4–8.0	Yellow	Red	0.1 g in 28.2 mL 0.01 M NaOH. Then add ~225 mL H ₂ O.
Neutral red	6.8–8.0	Red	Yellow	0.01 g in 50 mL ethanol. Then add 50 mL H ₂ O.
Cresol red	7.2–8.8	Yellow	Red	See above.
α-Naphtholphthalein	7.3–8.7	Pink	Green	0.1 g in 50 mL ethanol. Then add 50 mL H ₂ O.
Cresol purple	7.6–9.2	Yellow	Purple	See above.
Thymol blue	8.0–9.6	Yellow	Blue	See above.
Phenolphthalein	8.0–9.6	Colorless	Red	0.05 g in 50 mL ethanol. Then add 50 mL H ₂ O.
Thymolphthalein	8.3–10.5	Colorless	Blue	0.04 g in 50 mL ethanol. Then add 50 mL H ₂ O.
Alizarin yellow	10.1–12.0	Yellow	Orange-red	0.01 wt% in H ₂ O
Nitramine	10.8–13.0	Colorless	Orange-brown	0.1 g in 70 mL ethanol. Then add 30 mL H ₂ O.
Tropaeolin O	11.1–12.7	Yellow	Orange	0.1 wt% in H ₂ O.

Table 11-4
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The difference between the end point (point of detected color change) and the true equivalence point is the *indicator error*

Amount of indicator added should be negligible

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Questions:

1) What is the molarity of a nitric acid solution if 43.33 mL of 0.1000 M KOH solution is needed to neutralize 20.00 mL of the acid solution?

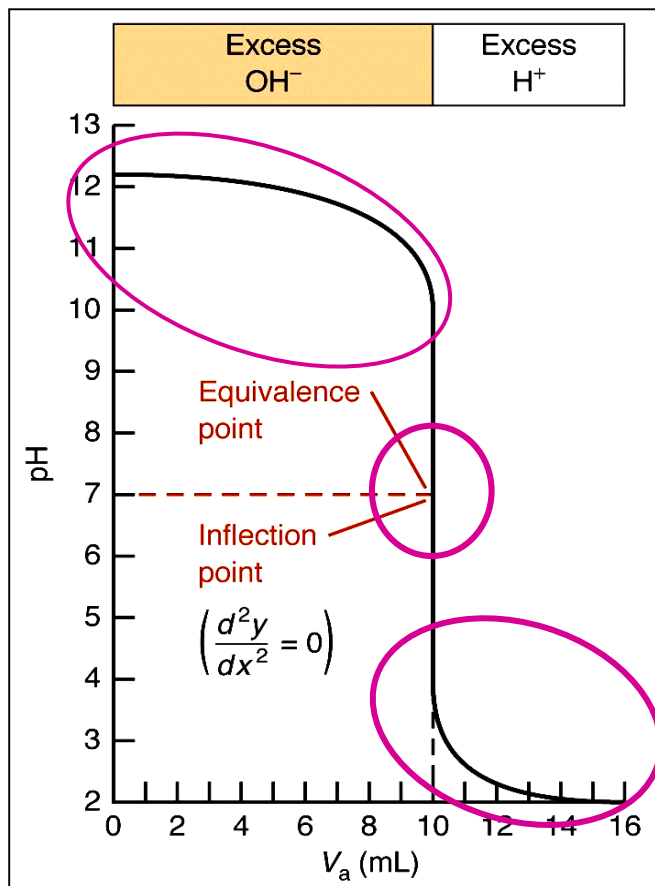
- 2) What is the concentration of a household ammonia cleaning solution if 49.90 mL of 0.5900 M HCl is required to neutralize 25.00 mL of the solution?
- 3) How many milliliters of 0.500 M NaOH would neutralize 25.00 mL of 0.100 M H₂SO₄?

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Example 1: Titrate of 50.00 ml of 0.02000 M KOH with 0.1000 M HBr.

1) Calculate volume of HBr needed to reach the equivalence point, V_{eq}

$$\begin{aligned}\text{mmoles of KOH} &= \text{mmoles of HBr} \\ 0.02000 \text{ M} \times 50.00 \text{ mL} &= 0.1000 \text{ M} \times V_e \\ V_{eq} &= 10.00 \text{ mL}\end{aligned}$$



There are **3** parts to the titration curve:

1) **Before reaching the equivalence point**

→ excess OH⁻ present

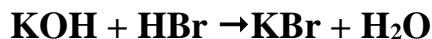
2) **At the equivalence point**

→ $[H^+] = [OH^-]$

3) **After reaching the equivalence point**

→ excess H⁺ present

2) Calculate the pH after adding 2.00 mL HBr



Initial mmoles 1.00 0.20

Final mmoles 0.80 0.00

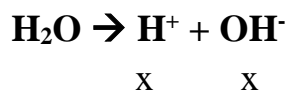
$$[\text{OH}^-] = 0.80 \text{ mmol} / 52.00 \text{ mL} = 0.0154 \Rightarrow \text{pOH} = 1.81 \Rightarrow \text{pH} = 12.19$$

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3) Calculate the pH at the equivalence point

At the equivalence point \rightarrow moles of H^+ = moles of OH^-

pH is determined by dissociation of H_2O :



$$K_w = [\text{H}^+][\text{OH}^-]$$

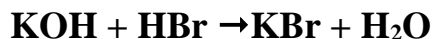
$$1 \times 10^{-14} = x^2$$

$$x = 1 \times 10^{-7} \text{ M} \Rightarrow [\text{H}^+] = 1 \times 10^{-7} \text{ M} \Rightarrow \text{pH} = 7.00$$

pH = 7 at the equivalence point ONLY for strong acid – strong base titrations!!

4) Calculate the pH after adding 10.10 mL HBr

After reaching the equivalence point \rightarrow excess H^+ present



Initial mmoles 1.00 1.01

Final mmoles 0.00 0.01

$$[\text{HBr}] = 0.01 \text{ mmol} / 60.1 \text{ mL} = 1.66 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.78$$

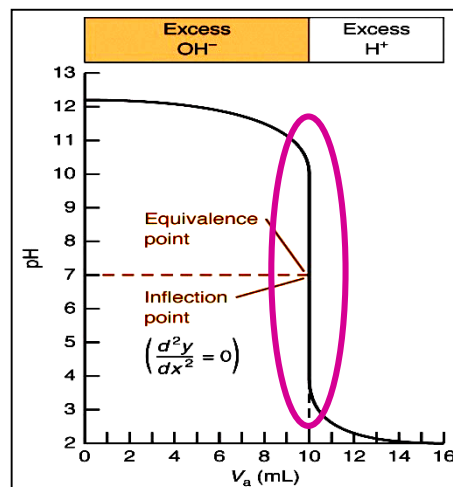
Note:

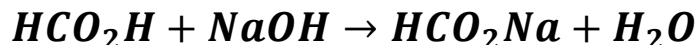
A rapid change in pH near the equivalence point occurs.

Equivalence point where:

- slope is greatest

$$\text{slope} = \frac{d\text{pH}}{dV_a}$$



Example 2: TITRATION OF WEAK ACID WITH STRONG BASE**Titrate 50.00 mL of 0.02000 M formic acid with 0.1000 M NaOH.****HA****A⁻**

$$K = \frac{1}{K_b} = 1.80 \times 10^{10}$$

Equilibrium constant so large \Rightarrow reaction “goes to completion” after each addition of OH⁻ (strong and weak react completely)

$$K_a(\text{HA}) = 1.80 \times 10^{-4} \quad \Rightarrow \quad \text{p}K_a = 3.745$$

$$K_b(\text{A}^-) = 5.56 \times 10^{-11}$$

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Calculate volume of NaOH needed to reach the equivalence point, V_{eq}

$$\text{mmoles of HCO}_2\text{H} = \text{mmoles of KOH}$$

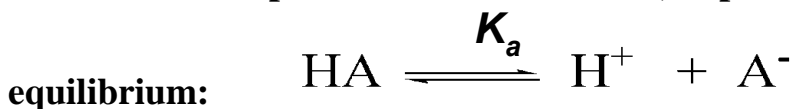
$$0.02000 \text{ M} \times 50.00 \text{ mL} = 0.1000 \text{ M} \times V_e$$

$$V_{\text{eq}} = 10.00 \text{ mL}$$

There are 4 parts to the titration curve:

1) Before base is added

\rightarrow HA and H₂O present. HA = weak acid, \therefore pH determined by



At equilibrium $0.020 - x \qquad x \qquad x$

$$1.80 \times 10^{-4} = \frac{x^2}{0.020 - x}$$

$$x^2 + 1.80 \times 10^{-4} x - 3.60 \times 10^{-6} = 0$$

$$x = 1.81 \times 10^{-3}$$

$$\therefore [\text{H}^+] = 1.81 \times 10^{-3} \Rightarrow \text{pH} = 2.74$$

- 2) From first addition of NaOH to immediately before equivalence point
 → mixture of unreacted HA and A⁻. BUFFER!! ∴ use Henderson-Hasselbalch equation for pH

Calculate the pH after adding 2.00 ml NaOH

	$\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$		
Initial mmoles	1.00	0.20	0.00
Final mmoles	0.80	0.00	0.20

$$\text{pH} = \text{pK}_a + \log \frac{n_{\text{A}^-}}{n_{\text{HA}}} \quad \text{pH} = 3.745 + \log \frac{0.20}{0.80} = 3.14$$

When volume of titrant = $\frac{1}{2} V_{\text{eq}}$ (after adding 5.00 ml NaOH)

$\text{pH} = \text{pK}_a$ Since: *moles of HA = moles of A⁻*

- 3) At the equivalence point after adding 10.00 mL of NaOH ($n_{\text{HA}} = n_{\text{NaOH}}$)
 → all HA converted to A⁻. A⁻ = weak base.



Initial mmoles 1.00 1.00 0.00

Final mmoles 0.00 0.00 1.00

$$[\text{A}^-] = \frac{1.00 \text{ mmol}}{60.00 \text{ mL}} = 0.0167 \text{ M}$$

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∴ **Solution contains just A⁻ ⇒ a solution of weak base**

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$5.56 \times 10^{-11} = \frac{x^2}{0.0167 - x}$$

$$[\text{OH}^-] = 9.63 \times 10^{-7} \text{ M} \rightarrow \text{pOH} = 6.02 \rightarrow \text{pH} = 7.98$$

pH is slightly basic (pH above 7) for strong base-weak acid titrations

Problem: Calculate the pH during the titration of 20.00 mL of 0.250 M nitrous acid (HNO₂; $K_a = 4.5 \times 10^{-4}$) after adding different volumes of 0.150 M NaOH : (a) 0.00 mL (b) 15.00 mL (c) 20.00 mL (d) 35.00 mL.

Answers: (a) 1.97 (b) 3.26 (c) 3.53 (d) 11.66