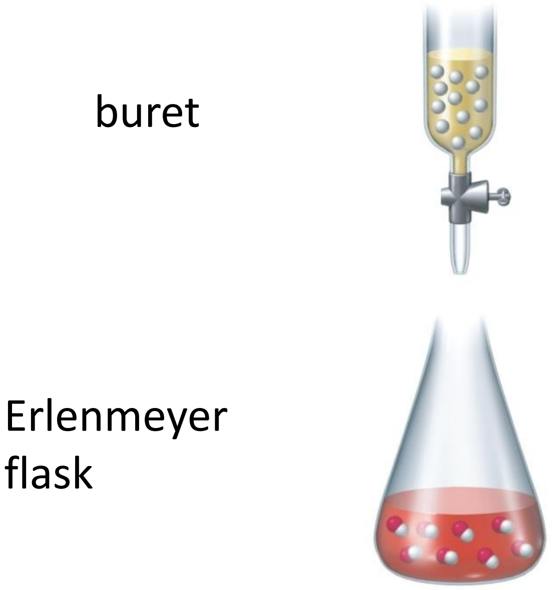
Ch 16 Aqueous Ionic Equilibrium

(Buffers and Acid/BaseTitration)



Problem 3-23 Chemistry, 5/e

Modified By Dr. Cheng-Yu Lai

Review- Reaction of Weak Bases/Acids with Water

The generic reaction for a base reacting with water, producing its conjugate acid and hydroxide ion:

$$B + H_2O \leftrightarrows BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

How about Weak acids with water ? What is Ka ?

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

Buffer Solutions

Buffer Solution: A solution which contains a weak acid and its conjugate base and resists drastic changes in pH.

Weak acid

\+

Conjugate base

For Example:

- CH_3CO_2H + $CH_3CO_2^{1-}$
- HF + F^{1-}
- NH_4^{1+} + NH_3
- $H_2PO_4^{2-}$ + HPO_4^{2-}

Buffered solutions contain either:

A weak acid and its salt (conjugate base)
A weak base and its salt (conjugate acid)

Buffer Solution Preparation

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + CH_3CO_2^{1-}(aq)$$

Weak acid

Conjugate base
($NaCH_3CO_2$)

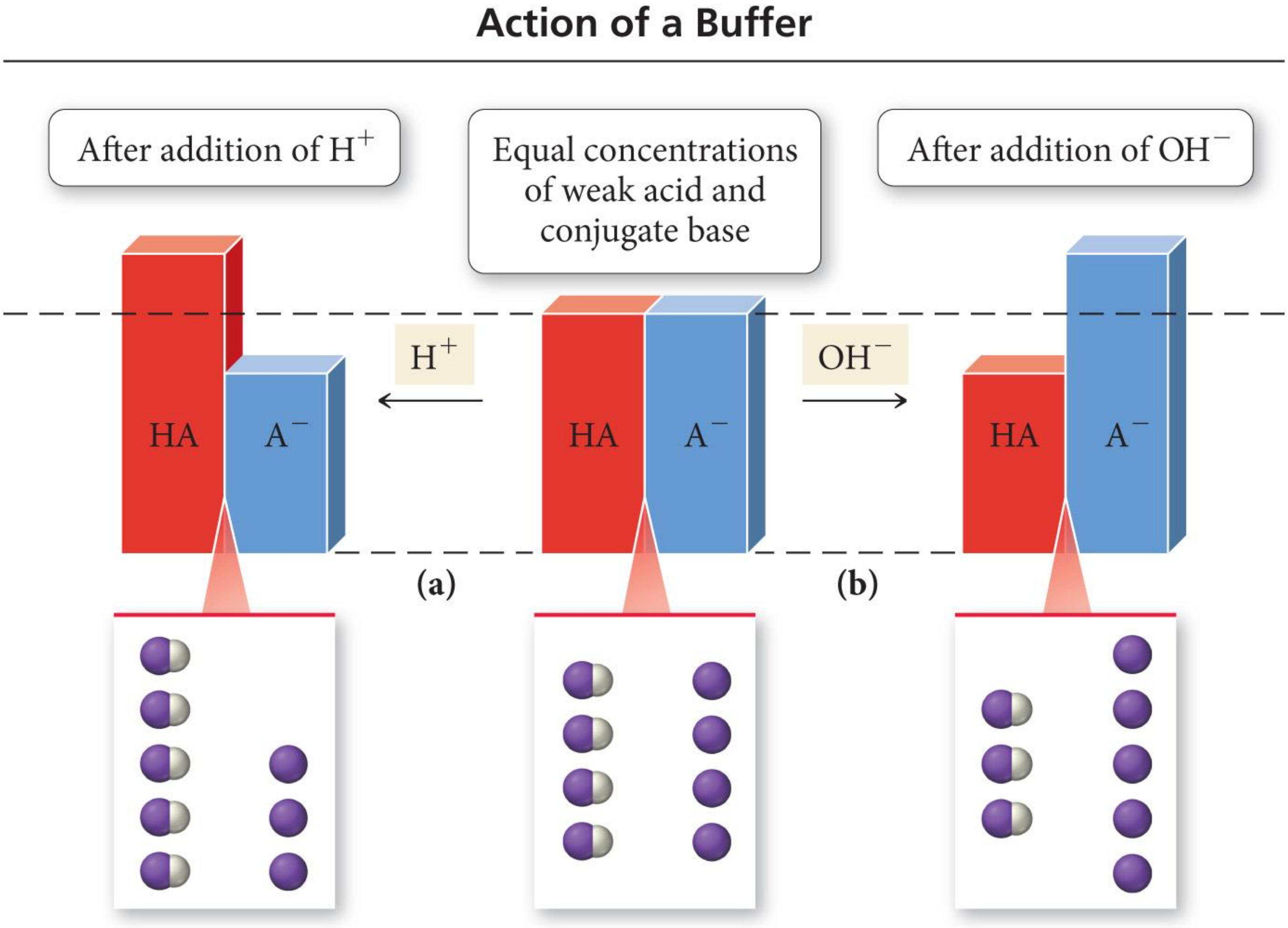
Addition of OH^{1-} to a buffer:

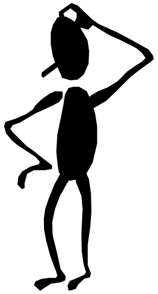
$$CH_3CO_2H(aq) + OH^{1-}(aq) \xrightarrow{100\%} H_2O(l) + CH_3CO_2^{1-}(aq)$$

Addition of H_3O^{1+} to a buffer:

$$CH_3CO_2^{1-}(aq) + H_3O^{1+}(aq) \xrightarrow{100\%} H_2O(l) + CH_3CO_2H(aq)$$

Action of a Buffer





Which of the following are buffer systems? (a) KF/HF (b) KBr/HBr, (c) Na_2CO_3/$NaHCO_3$ (d) HCl/NaCl

(a) HF is a weak acid and F^- is its conjugate base

(b) HBr is a strong acid ; same as d

(c) CO_3^{2-} is a weak base and HCO_3^- is its conjugate acid

Buffered solutions contain either:

a. A weak acid and its salt
b. A weak base and its salt

Why buffer works ? Common-Ion Effect: The *shift in the position of an equilibrium* on addition of a substance that provides an ion in common with one of the ions already involved in the equilibrium.

The pH of 0.10 M acetic acid is 2.89. Calculate the pH of a solution that is prepared by dissolved 0.10 mol of acetic acid and 0.10 mol sodium acetate in enough water to make 1.00 L of solution.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + CH_3CO_2^{1-}(aq)$$

I	0.10		≈0	0.10
C	-x		+x	+x
E	0.10 - x		x	0.10 + x

$$K_\mathbf{a} = \frac{[H_3O^{1+}][CH_3CO_2^{1-}]}{[CH_3CO_2H]} \quad \mathbf{= 1.8 \times 10^{-5}}$$

The Common-Ion Effect

$$1.8 \times 10^{-5} = \frac{(x)(0.10 + x)}{(0.10 - x)} \approx \frac{x(0.10)}{0.10}$$

$$x = [H_3O^{1+}] = 1.8 \times 10^{-5}\ M$$

$$\text{pH} = -\log([H_3O^{1+}]) = -\log(1.8 \times 10^{-5}) = \boxed{4.74}$$

Why is there a difference in pH?

Le Châtelier’s Principle

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + CH_3CO_2^{1-}(aq)$$

The addition of acetate ion to a solution of acetic acid suppresses the dissociation of the acid. The equilibrium shifts to the left.

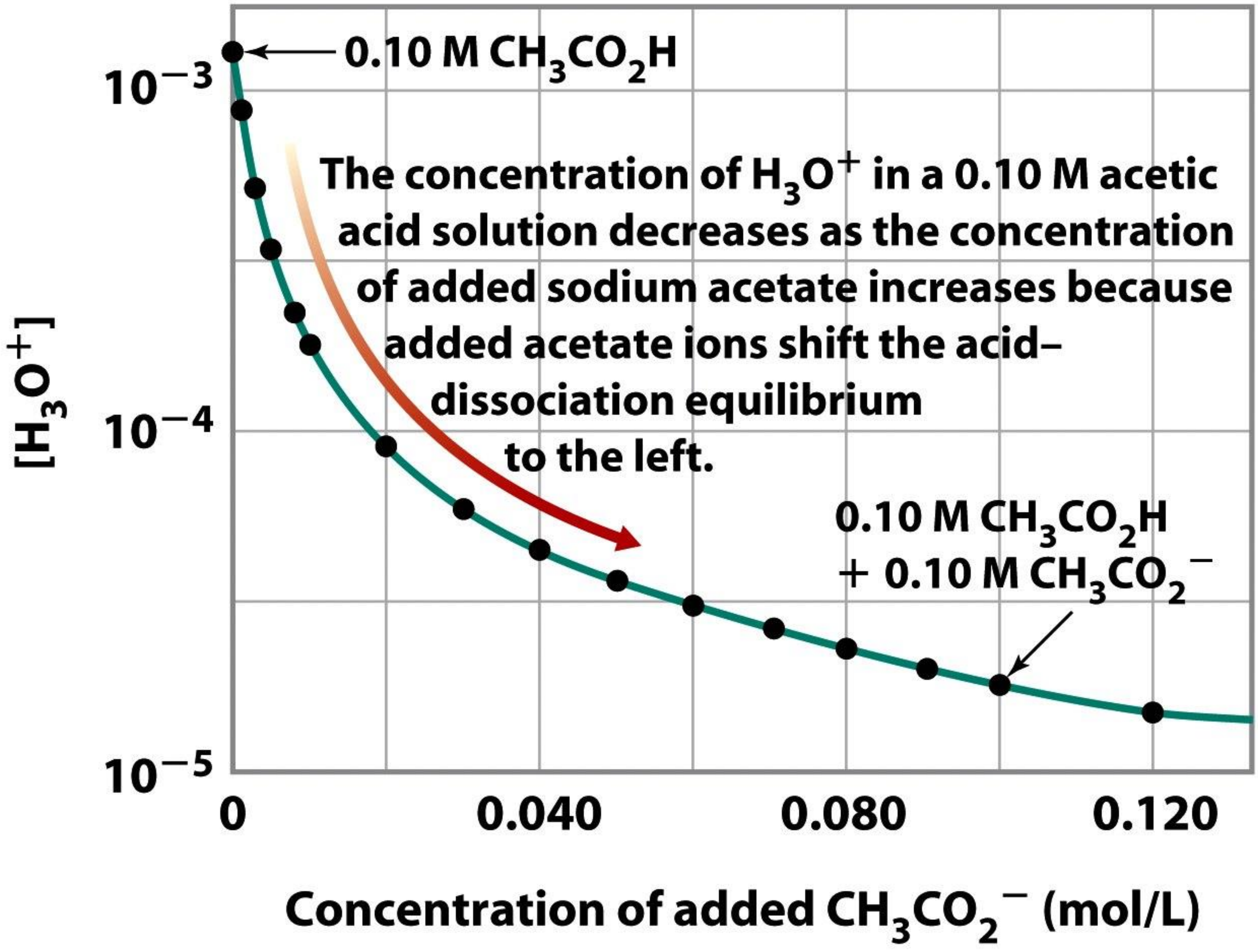


Figure 15-2 Chemistry, 5/e

Common Ion

1. Ion provided in solution by an aqueous acid (or base) as well as a salt
    a. HF(aq) and NaF (F$^-$ in common)

    $$HF(aq) \bullet H^+(aq) + F^-(aq)$$ *Excess F$^-$ added by NaF*

    $$\longleftarrow$$

    Equilibrium shifts away from added component. Fewer H$^+$ ions present. pH is higher than expected.

    b. NH_4OH and NH_4Cl (NH_4^+ in common)

    $$NH_3(aq) + H_2O(l) \bullet NH_4^+(aq) + OH^-(aq)$$

    $$\longleftarrow$$

    Equilibrium shifts to the left. pH of the solution decreases due to a decrease in OH$^-$ concentration

- Adding a salt containing the anion NaA, which is the conjugate base of the acid (the common ion), shifts the position of equilibrium to the left.

$$HA_{(aq)} + H_2O_{(l)} \Leftrightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

$$\longleftarrow$$

- This causes the pH to be higher than the pH of the acid solution, lowering the H_3O^+ ion concentration.

Example 16.2 Calculating the pH of a Buffer Solution as an Equilibrium Problem and with the Henderson–Hasselbalch Equation

Calculate the pH of a buffer solution that is 0.050 M in benzoic acid ($HC_7H_5O_2$) and 0.150 M in sodium benzoate ($NaC_7H_5O_2$). For benzoic acid, $K_a = 6.5 \times 10^{-5}$.

Solution

Write the balanced equation for the ionization of the acid and use it as a guide to prepare an ICE table.

$$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$$

	$[HC_7H_5O_2]$	$[H_3O^+]$	$[C_7H_5O_2^-]$
Initial	0.050	≈ 0.00	0.150
Change	$-x$	$+x$	$+x$
Equil	$0.050 - x$	x	$0.150 + x$

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]}$$

$$= \frac{x(0.150 + \cancel{x})}{0.050 - \cancel{x}} \qquad (x \text{ is small})$$

$$6.5 \times 10^{-5} = \frac{x(0.150)}{0.050}$$

$$x = 2.2 \times 10^{-5}$$

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(2.2 \times 10^{-5}) \\ &= 4.66 \end{aligned}$$

$$\frac{2.2 \times 10^{-5}}{0.050} \times 100\% = 0.044\%$$

Large Ka has greatest percent ionization

The Henderson-Hasselbach Equation

derivation

Generic weak acid

Conjugate base

$$\mathrm{HA} + \mathrm{H_2O} \Leftrightarrow \mathrm{H_3O^+} + \mathrm{A^-}$$

$$K_a = [\mathrm{H_3O^+}]\,[\mathrm{A^-}]/[\mathrm{HA}]$$

$$pK_a = -\log K_a = -\log([\mathrm{H_3O^+}]\,[\mathrm{A^-}]/[\mathrm{HA}])$$

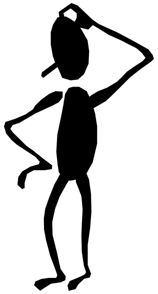
$$\mathrm{Log}\ xy = \log x + \log y$$

$$pK_a = -\log[\mathrm{H_3O^+}] - \log([\mathrm{A^-}]/[\mathrm{HA}])$$

$$pK_a = pH - \log([\mathrm{A^-}]/[\mathrm{HA}])$$

$$pH = pK_a + \log([\mathrm{A^-}]/[\mathrm{HA}])$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\text{Conjugate Base}]}{[\text{Acid}]}\right)$$



What is the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK? Ka = 1.8E-4

Mixture of weak acid and conjugate base!

	$HCOOH\ (aq)$	$\rightleftharpoons$	$H^+\ (aq)$	$+\ HCOO^-\ (aq)$
Initial (M)	0.30		0.00	0.52
Change (M)	$-x$		$+x$	$+x$
Equilibrium (M)	$0.30 - x$		x	$0.52 + x$

***Common ion effect* – X small**

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

$0.30 - x \approx 0.30$

$0.52 + x \approx 0.52$

$$\mathrm{pH} = 3.77 + \log\frac{[0.52]}{[0.30]} = \underline{\quad\text{EXAM}\qquad}$$

HCOOH pK_a = 3.77

Buffer Capacity and Range

1. A solution that resists a change in pH when either hydroxide ions <u>or</u> protons are added.

   the effective pH range of a buffer is pK_a ± 1.

A buffer will be effective when 0.1 < [base]:[acid] < 10.

$$pH = pK_a + \log(0.10)$$

$$pH = pK_a - 1$$

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

$$pH = pK_a + \log(10)$$

$$pH = pK_a + 1$$

2. A buffer is most effective when pH = pK.

   At this pH [acid] = [conjugate base].

   The buffer is equally effective against added acid or added base.

3. The buffer loses effectiveness when added acid/base exceeds the [buffer].

When choosing an acid to make a buffer, choose one whose pK_a is closest to the pH of the buffer.

pH Titration Curves

Titration: A procedure for determining the concentration of a solution by allowing a carefully measured volume to react with a solution of another substance (the standard solution) whose concentration is known.

Problem 3-23 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

buret

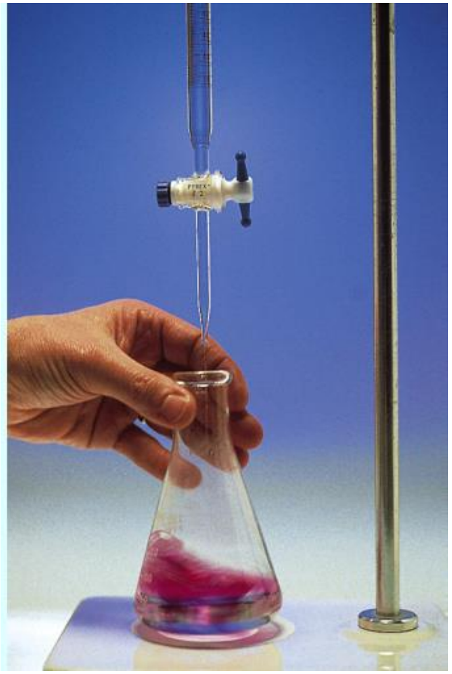
standard solution
(known concentration)

Erlenmeyer
flask

unknown concentration solution

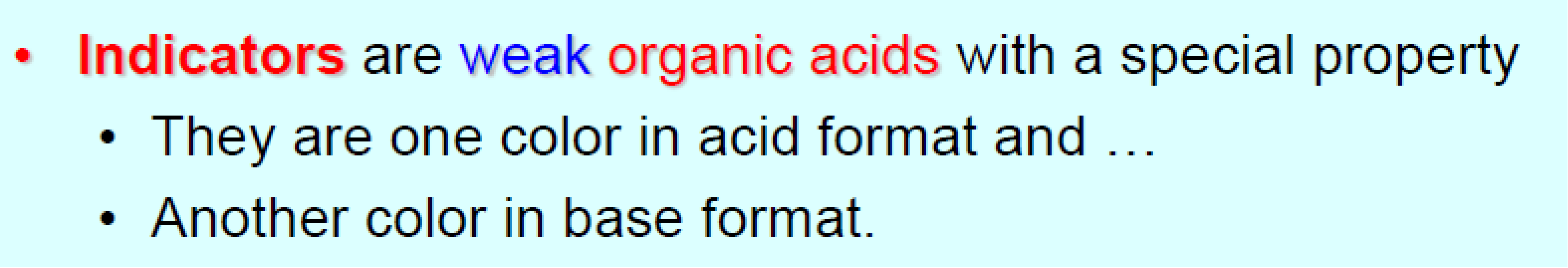
An indicator is added which changes color once the reaction is complete

Titration, Titration Curves and Indicators



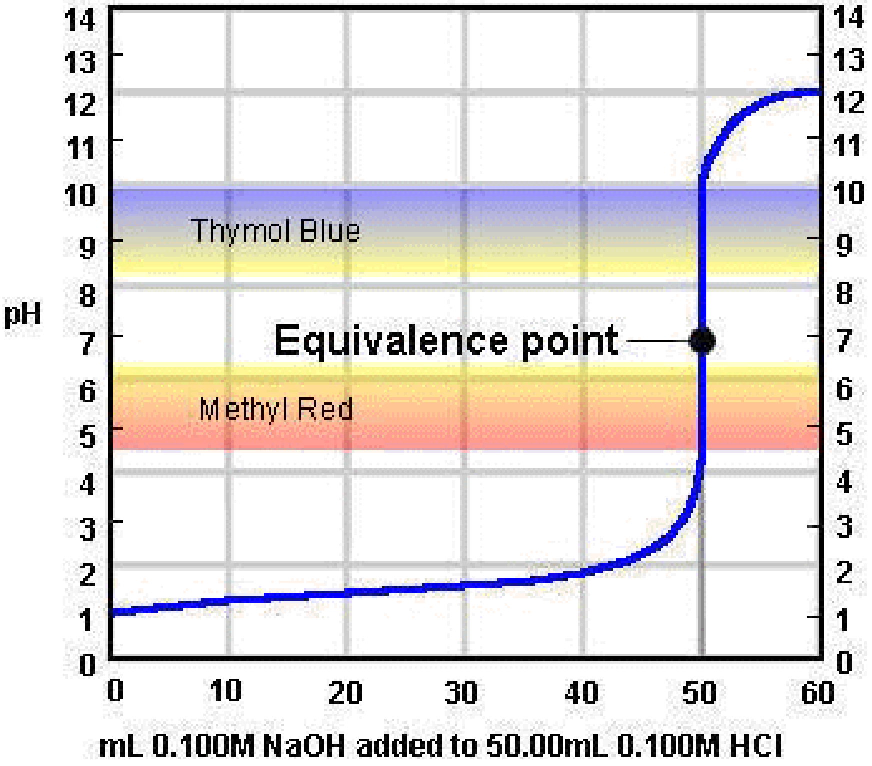
Acid / conjugate base and indicator or Base/conjugated acid and indicator

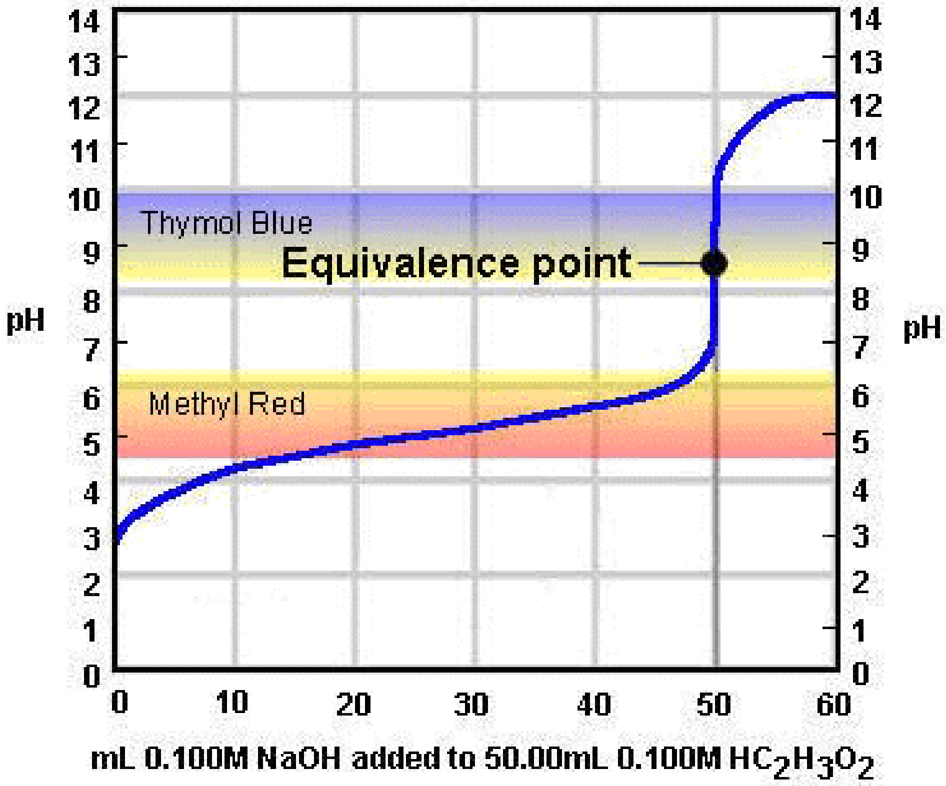
3. If we observe the resulting pH while titrating either a strong or a weak acid with a strong base, we can plot that data to get a titration curve.
4. The titration curve is sigmoidal in shape, with a steep rise in pH around the neutralization or equivalence point.



- **Indicators** are weak organic acids with a special property
  - They are one color in acid format and …
  - Another color in base format.

Selection of Indicators





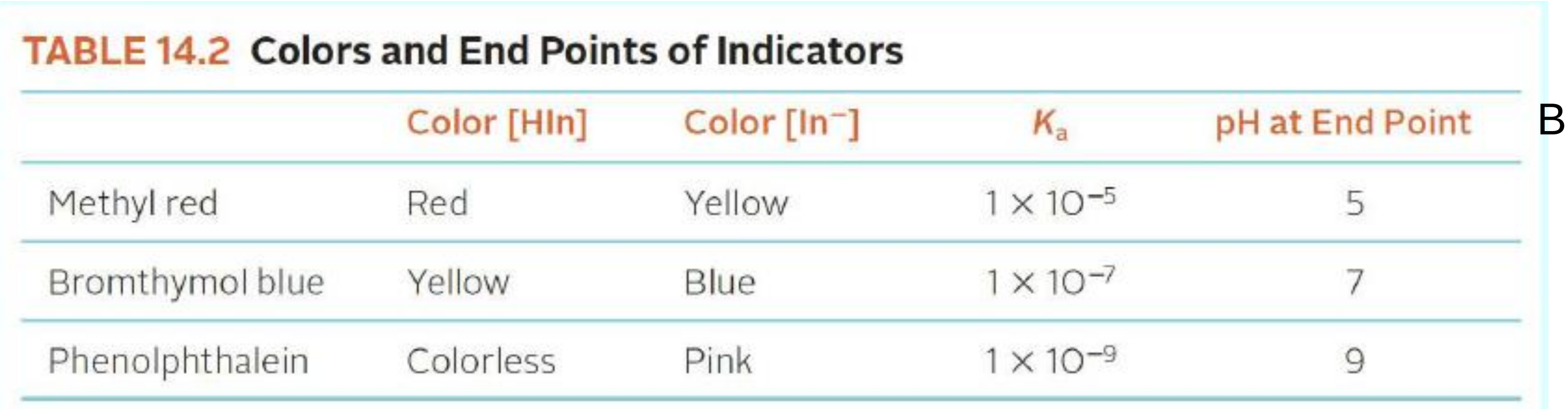


TABLE 14.2 Colors and End Points of Indicators

	Color [HIn]	Color [In⁻]	K_a	pH at End Point
Methyl red	Red	Yellow	1×10^{-5}	5
Bromthymol blue	Yellow	Blue	1×10^{-7}	7
Phenolphthalein	Colorless	Pink	1×10^{-9}	9

Buffer Range

4±6

6±8

8±10

Acid-Base Indicators

- An acid-base indicator is useful in determining the **equivalence point** in a **titration.**
  - The point at which **exact neutralization** has occurred is called the **equivalence point**.
  - The point at which the indicator changes color is called the **endpoint**.

The equivalence point and the endpoint should overlap or at least near with each other.

Indicators as Weak Organic Acids

- **Indicators** are weak organic acids with a special property
  - They are one color in acid format and …
  - Another color in base format.

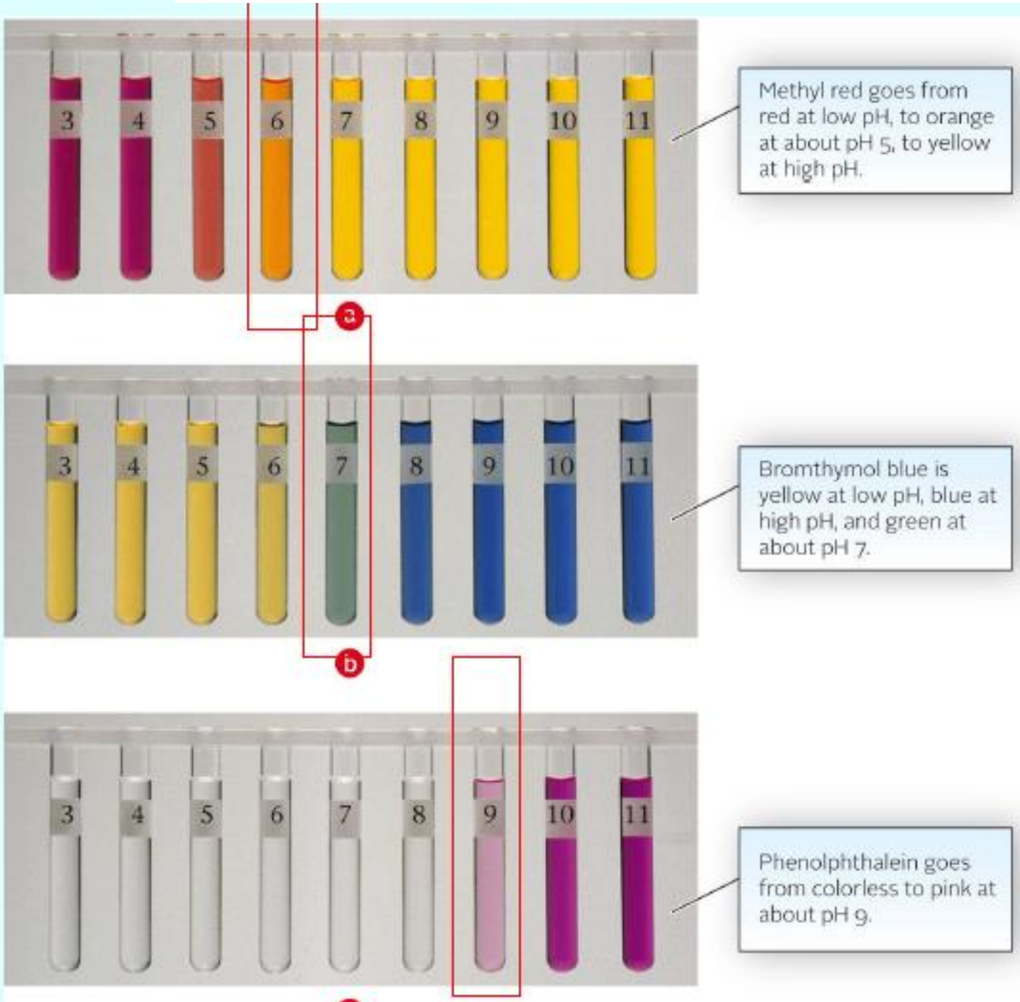
- We can write the formula for an indicator as **Hin** as acid format.
- Equilibrium for HIn is the same as for any other weak acid
  - $HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$

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

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

Which Color?

- The color of the indicator is controlled by $[H^+]$, which determines [HIn]/[In]
- If $\frac{[HIn]}{[In^-]} \geq 10$ the indicator will be the acid (**HIn**) color
- If $\frac{[HIn]}{[In^-]} \leq 0.10$ the indicator will be the base (**In⁻**) color
- If $\frac{[HIn]}{[In^-]} \approx 1$ the indicator will be an intermediate color



Methyl red goes from red at low pH, to orange at about pH 5, to yellow at high pH.

Bromthymol blue is yellow at low pH, blue at high pH, and green at about pH 7.

Phenolphthalein goes from colorless to pink at about pH 9.

Strong Acid-Strong Base Titrations

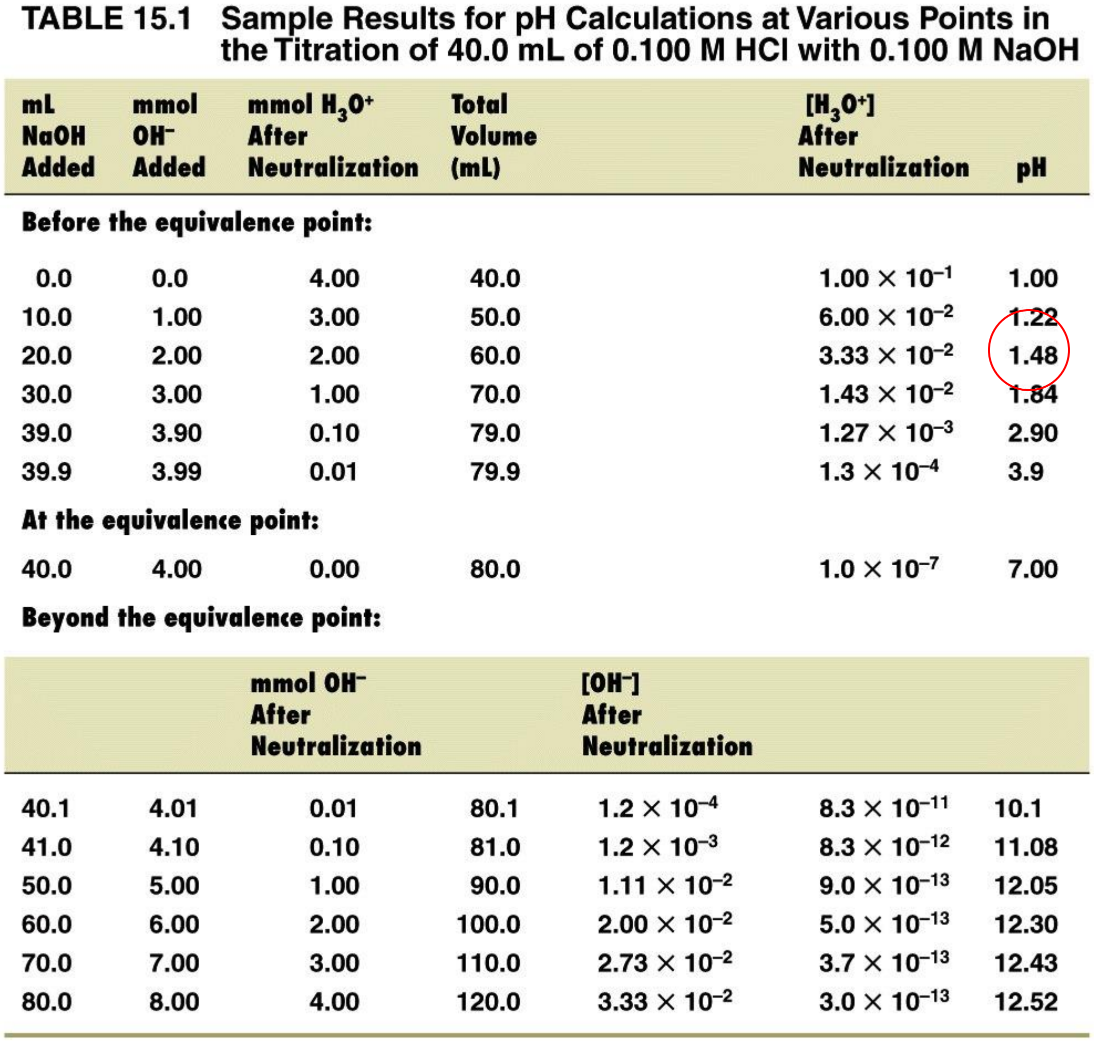
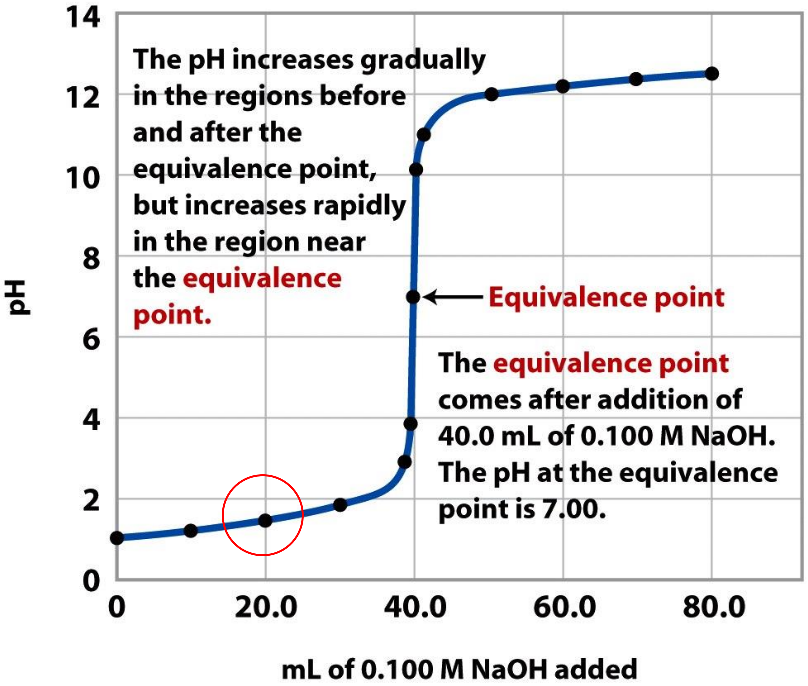


TABLE 15.1 Sample Results for pH Calculations at Various Points in the Titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH

mL NaOH Added	mmol OH^- Added	mmol H_3O^+ After Neutralization	Total Volume (mL)	$[H_3O^+]$ After Neutralization	pH
Before the equivalence point:					
0.0	0.0	4.00	40.0	1.00×10^{-1}	1.00
10.0	1.00	3.00	50.0	6.00×10^{-2}	1.22
20.0	2.00	2.00	60.0	3.33×10^{-2}	1.48
30.0	3.00	1.00	70.0	1.43×10^{-2}	1.84
39.0	3.90	0.10	79.0	1.27×10^{-3}	2.90
39.9	3.99	0.01	79.9	1.3×10^{-4}	3.9
At the equivalence point:					
40.0	4.00	0.00	80.0	1.0×10^{-7}	7.00
Beyond the equivalence point:					

		mmol OH^- After Neutralization		$[OH^-]$ After Neutralization		
40.1	4.01	0.01	80.1	1.2×10^{-4}	8.3×10^{-11}	10.1
41.0	4.10	0.10	81.0	1.2×10^{-3}	8.3×10^{-12}	11.08
50.0	5.00	1.00	90.0	1.11×10^{-2}	9.0×10^{-13}	12.05
60.0	6.00	2.00	100.0	2.00×10^{-2}	5.0×10^{-13}	12.30
70.0	7.00	3.00	110.0	2.73×10^{-2}	3.7×10^{-13}	12.43
80.0	8.00	4.00	120.0	3.33×10^{-2}	3.0×10^{-13}	12.52

Table 15-1 Chemistry, 5/e

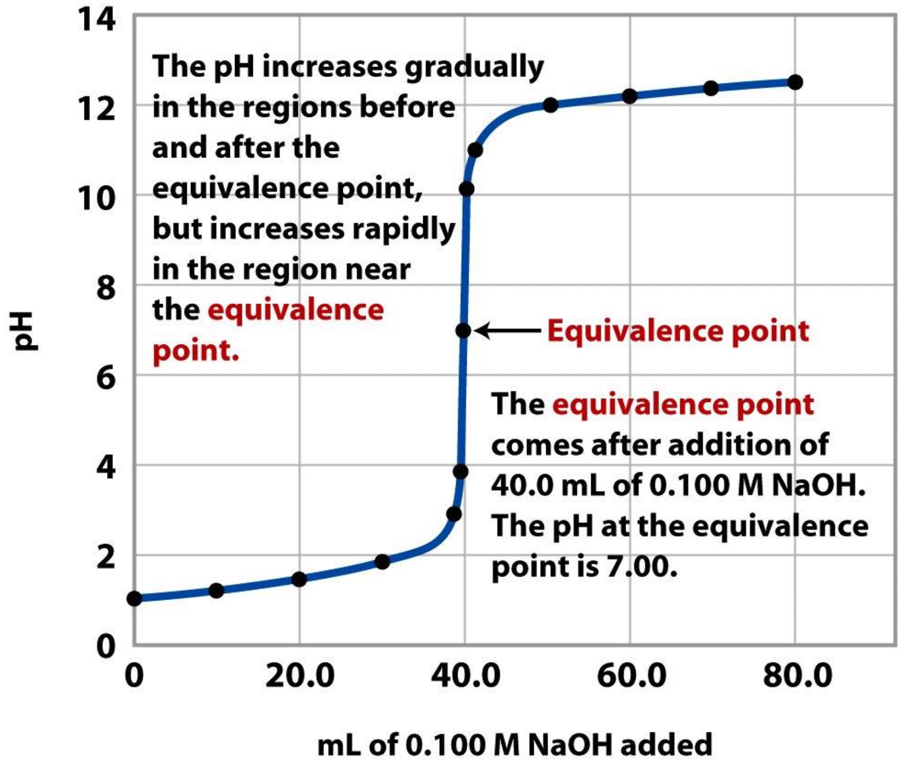


The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Figure 15-6b Chemistry, 5/e

Strong Acid-Strong Base Titrations

Equivalence Point: The point at which stoichiometrically equivalent quantities of acid and base have been mixed together.



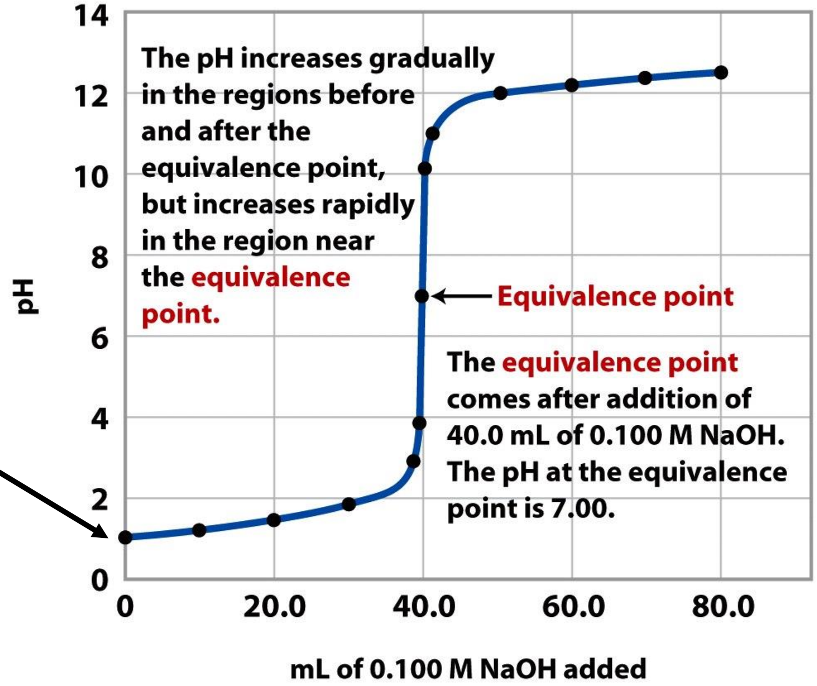
The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Figure 15-6b Chemistry, 5/e

Strong Acid-Strong Base Titrations

1. Before Addition of Any NaOH

0.100 M HCl



The pH increases gradually in the regions before and after the equivalence point, but increases rapidly in the region near the equivalence point.

The equivalence point comes after addition of 40.0 mL of 0.100 M NaOH. The pH at the equivalence point is 7.00.

The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

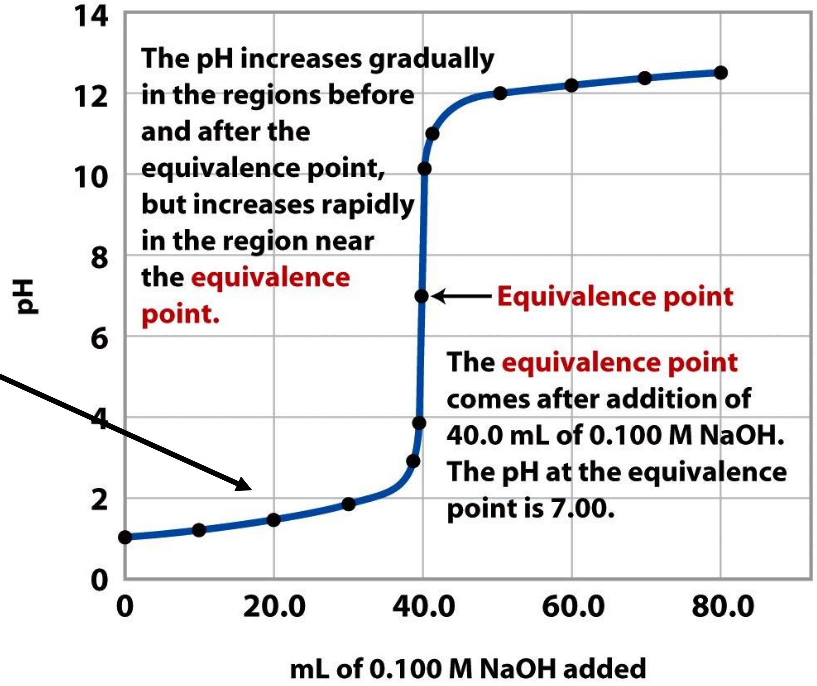
Figure 15-6b Chemistry, 5/e

Strong Acid-Strong Base Titrations

2. Before the Equivalence Point = ½ of [HCl] left

$$H_3O^{1+}(aq) + OH^{1-}(aq) \xrightarrow{100\%} 2H_2O(l)$$

Excess H_3O^{1+}



The pH increases gradually in the regions before and after the equivalence point, but increases rapidly in the region near the equivalence point.

The equivalence point comes after addition of 40.0 mL of 0.100 M NaOH. The pH at the equivalence point is 7.00.

The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

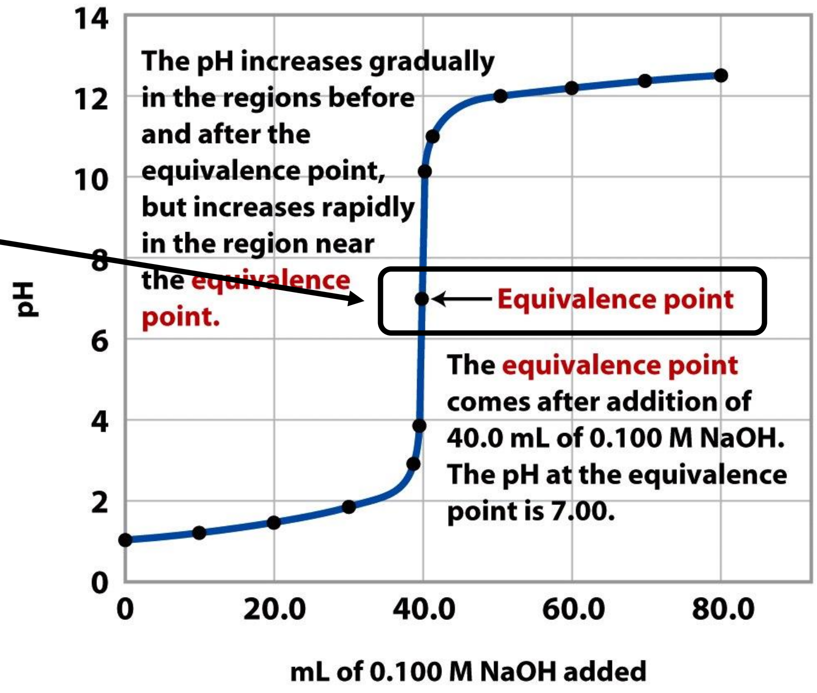
Figure 15-6b Chemistry, 5/e

Strong Acid-Strong Base Titrations

3. At the Equivalence Point

The quantity of H_3O^{1+} is equal to the quantity of added OH^{1-}.

pH = 7



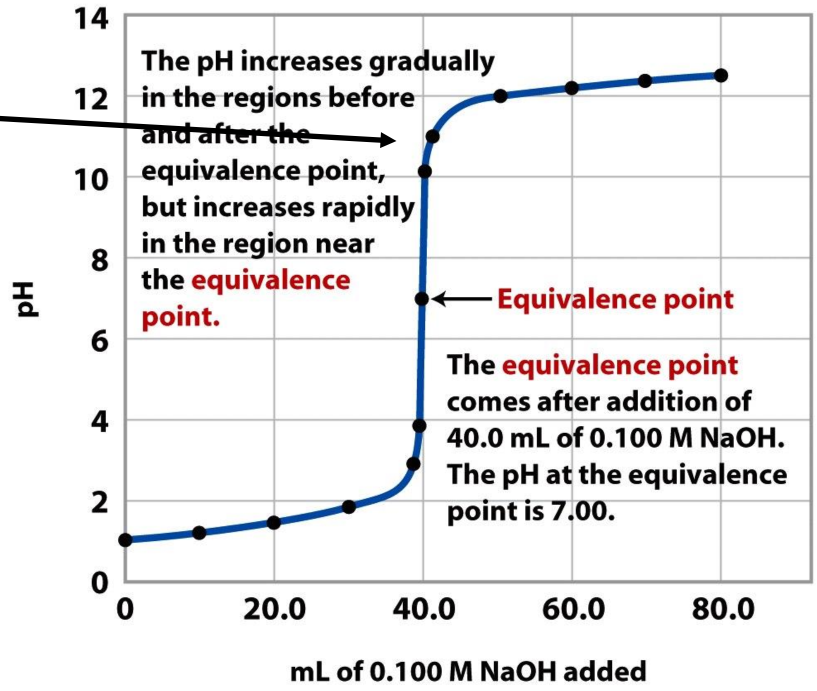
The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Figure 15-6b Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Strong Acid-Strong Base Titrations

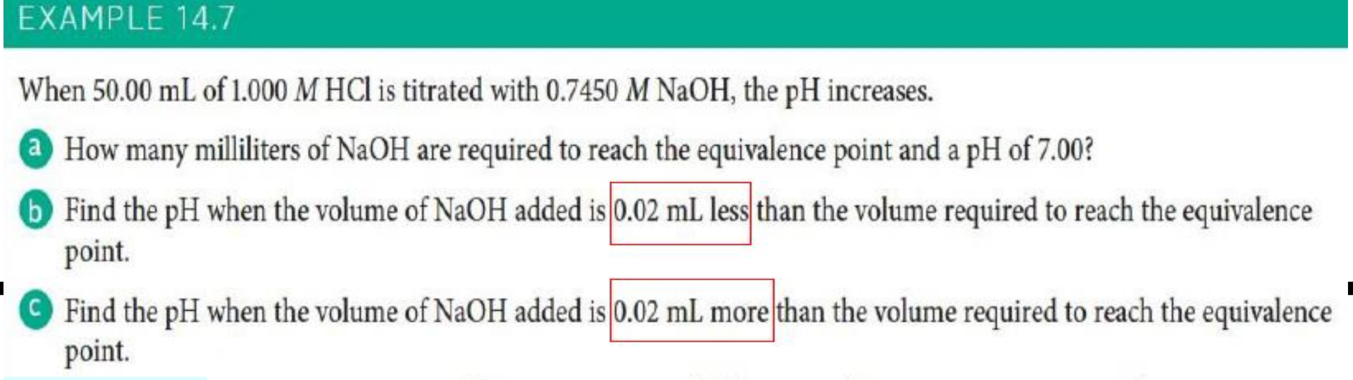
4. Beyond the Equivalence Point

Excess OH^{1-}



The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Figure 15-6b Chemistry, 5/e



EXAMPLE 14.7

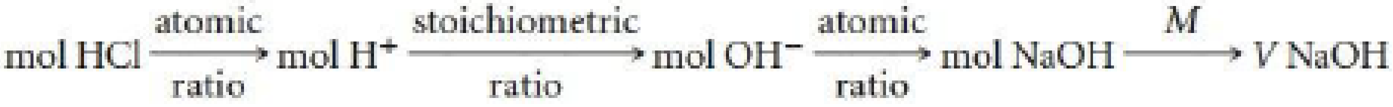
When 50.00 mL of 1.000 *M* HCl is titrated with 0.7450 *M* NaOH, the pH increases.

ⓐ How many milliliters of NaOH are required to reach the equivalence point and a pH of 7.00?

ⓑ Find the pH when the volume of NaOH added is 0.02 mL less than the volume required to reach the equivalence point.

ⓒ Find the pH when the volume of NaOH added is 0.02 mL more than the volume required to reach the equivalence point.

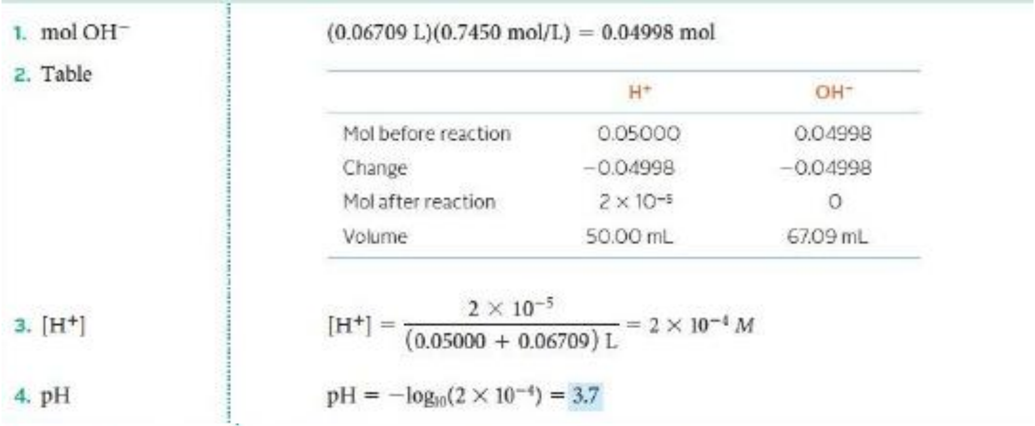
a. at equivalent poin



$$\text{mol HCl} \xrightarrow[\text{ratio}]{\text{atomic}} \text{mol H}^+ \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{mol OH}^- \xrightarrow[\text{ratio}]{\text{atomic}} \text{mol NaOH} \xrightarrow{M} V\ \text{NaOH}$$

acid mole = M1V1 = M2V2= base mole ⇒ V_{OH}= 67.11 ml

b. V_{OH} added = 67.09 ml



1. mol OH^- (0.06709 L)(0.7450 mol/L) = 0.04998 mol

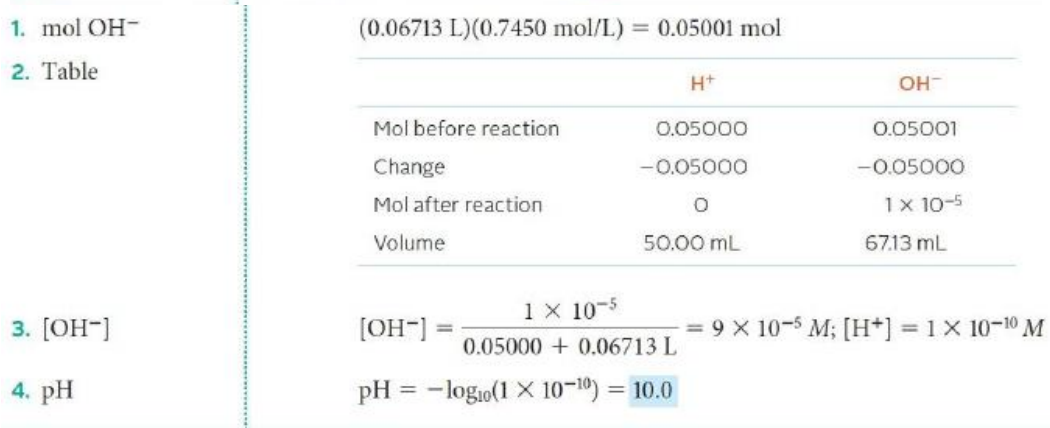
2. Table

	H^+	OH^-
Mol before reaction	0.05000	0.04998
Change	−0.04998	−0.04998
Mol after reaction	2×10^{-5}	0
Volume	50.00 mL	67.09 mL

3. $[H^+]$ $$[H^+] = \frac{2 \times 10^{-5}}{(0.05000 + 0.06709)\ \text{L}} = 2 \times 10^{-4}\ M$$

4. pH $$\text{pH} = -\log_{10}(2 \times 10^{-4}) = 3.7$$

c. V_{OH} added = 67.11 ml



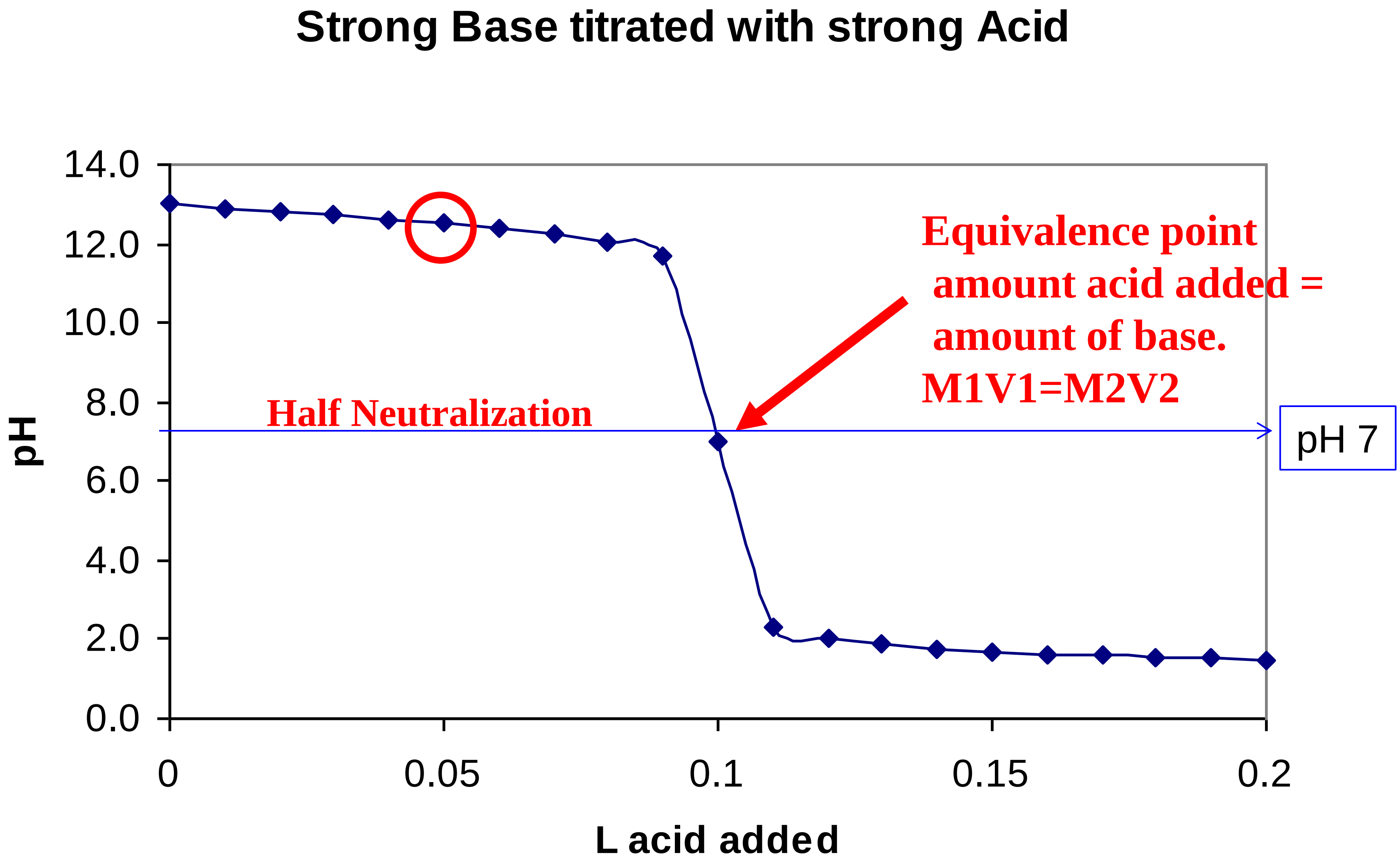
1. mol OH^- (0.06713 L)(0.7450 mol/L) = 0.05001 mol

2. Table

	H^+	OH^-
Mol before reaction	0.05000	0.05001
Change	−0.05000	−0.05000
Mol after reaction	0	1×10^{-5}
Volume	50.00 mL	67.13 mL

3. $[OH^-]$ $$[OH^-] = \frac{1 \times 10^{-5}}{0.05000 + 0.06713\ \text{L}} = 9 \times 10^{-5}\ M;\ [H^+] = 1 \times 10^{-10}\ M$$

4. pH $$\text{pH} = -\log_{10}(1 \times 10^{-10}) = 10.0$$



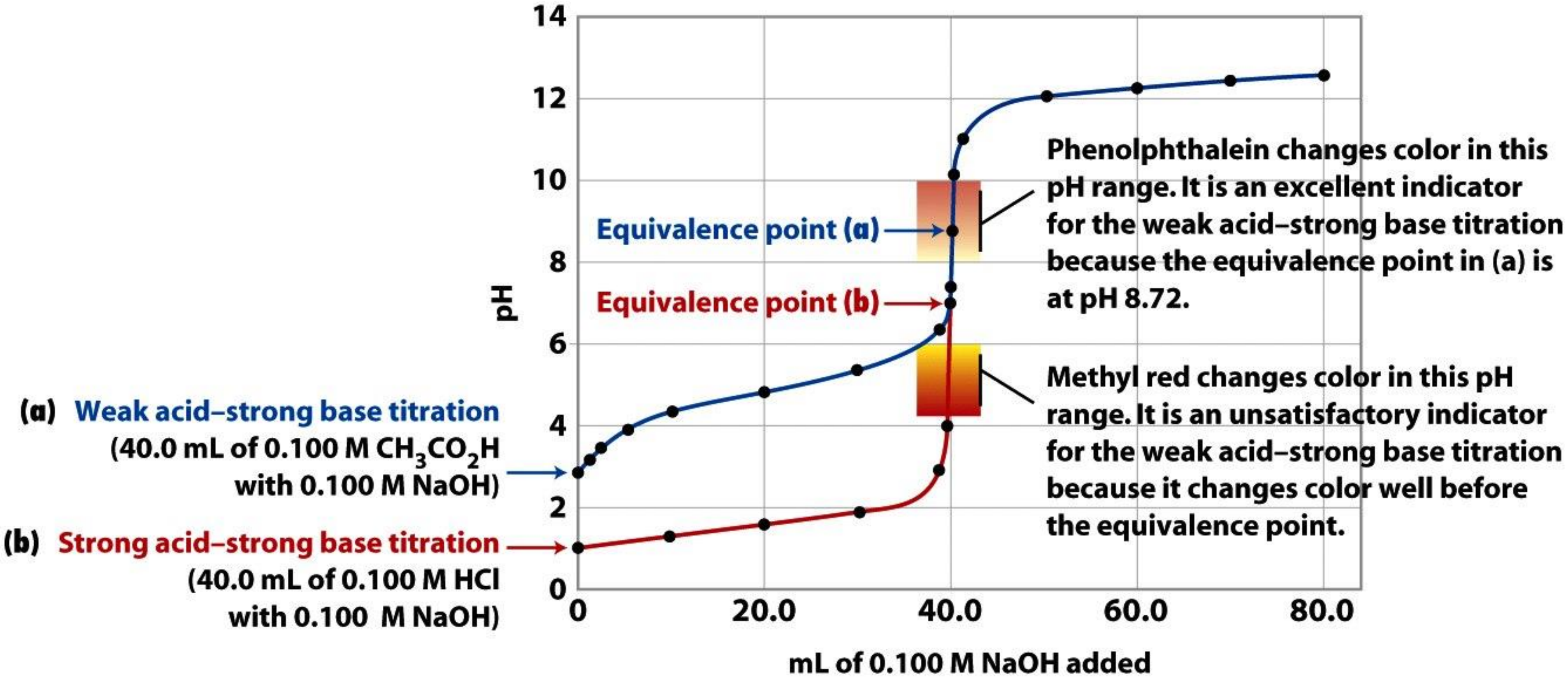
Strong Base titrated with strong Acid

Equivalence point
amount acid added =
amount of base.
M1V1=M2V2

Half Neutralization

Begin with 0.1 L of 0.1M NaOH - titrate with 0.1M HCl

Weak Acid-Strong Base Titrations



(a) Weak acid–strong base titration (40.0 mL of 0.100 M CH_3CO_2H with 0.100 M NaOH)

(b) Strong acid–strong base titration (40.0 mL of 0.100 M HCl with 0.100 M NaOH)

Phenolphthalein changes color in this pH range. It is an excellent indicator for the weak acid–strong base titration because the equivalence point in (a) is at pH 8.72.

Methyl red changes color in this pH range. It is an unsatisfactory indicator for the weak acid–strong base titration because it changes color well before the equivalence point.

Either phenolphthalein or methyl red can be used for the strong acid–strong base titration because the curve rises very steeply in the region of the equivalence point in (b) at pH 7.00.

Figure 15-8 Chemistry, 5/e

Weak Acid-Strong Base Titrations

1. **Before Addition of Any NaOH**

$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + CH_3CO_2^{1-}(aq)$

$0.100\ M\ CH_3CO_2H$

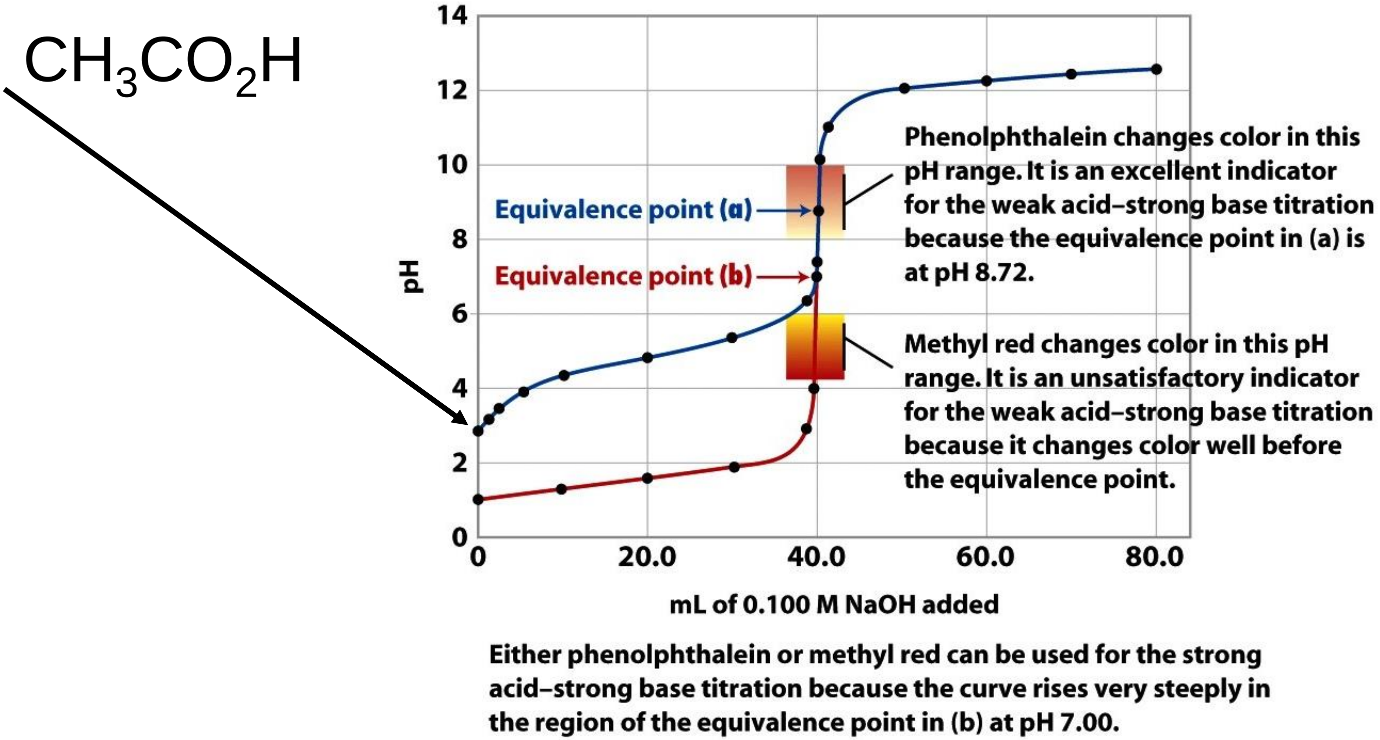


Figure 15-8 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

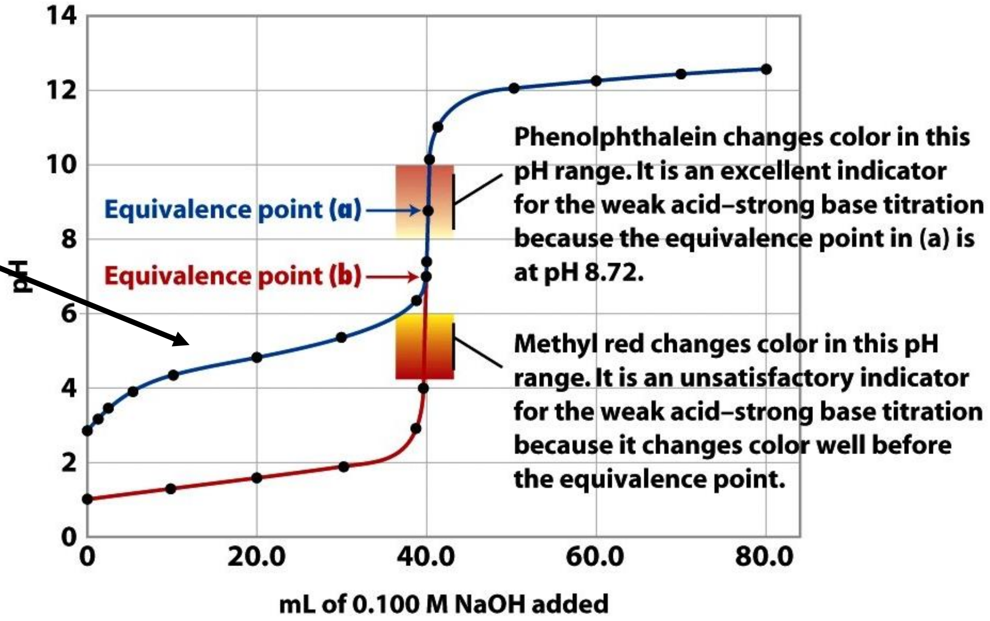
Weak Acid-Strong Base Titrations

2. Before the Equivalence Point

$$CH_3CO_2H(aq) + OH^{1-}(aq) \xrightarrow{100\%} H_2O(l) + CH_3CO_2^{1-}(aq)$$

Excess CH_3CO_2H

Half Neutralization
Buffer region
pH=pKa



Phenolphthalein changes color in this pH range. It is an excellent indicator for the weak acid–strong base titration because the equivalence point in (a) is at pH 8.72.

Methyl red changes color in this pH range. It is an unsatisfactory indicator for the weak acid–strong base titration because it changes color well before the equivalence point.

Either phenolphthalein or methyl red can be used for the strong acid–strong base titration because the curve rises very steeply in the region of the equivalence point in (b) at pH 7.00.

Figure 15-8 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

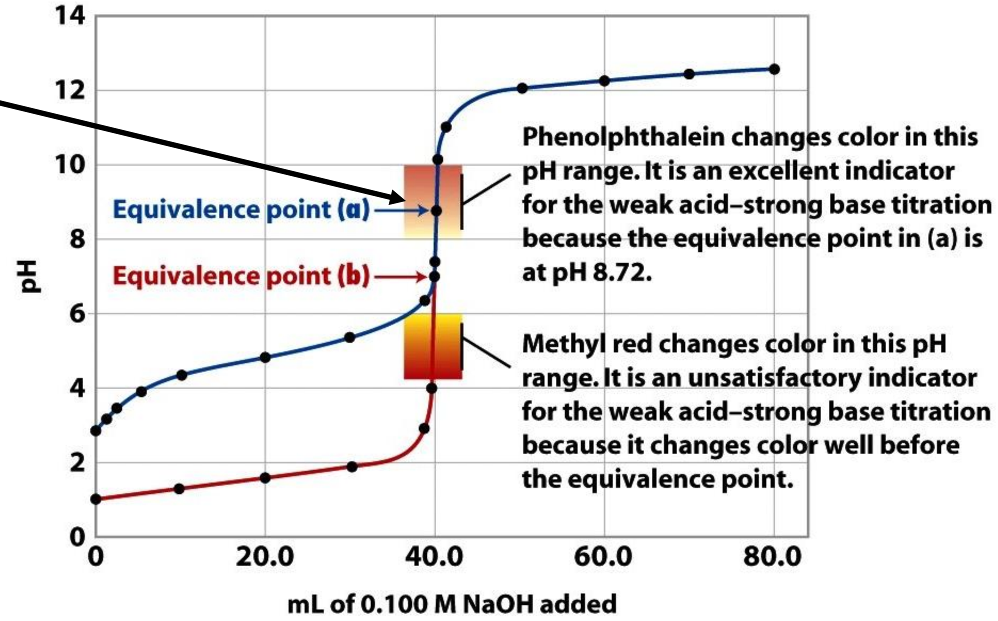
Weak Acid-Strong Base Titrations

3. At the Equivalence Point

$CH_3CO_2^{1-}(aq) + H_2O(l) \rightleftharpoons OH^{1-}(aq) + CH_3CO_2H(aq)$

pH > 7

Notice how the pH at the equivalence point is shifted up versus the strong acid titration.



Phenolphthalein changes color in this pH range. It is an excellent indicator for the weak acid–strong base titration because the equivalence point in (a) is at pH 8.72.

Methyl red changes color in this pH range. It is an unsatisfactory indicator for the weak acid–strong base titration because it changes color well before the equivalence point.

Either phenolphthalein or methyl red can be used for the strong acid–strong base titration because the curve rises very steeply in the region of the equivalence point in (b) at pH 7.00.

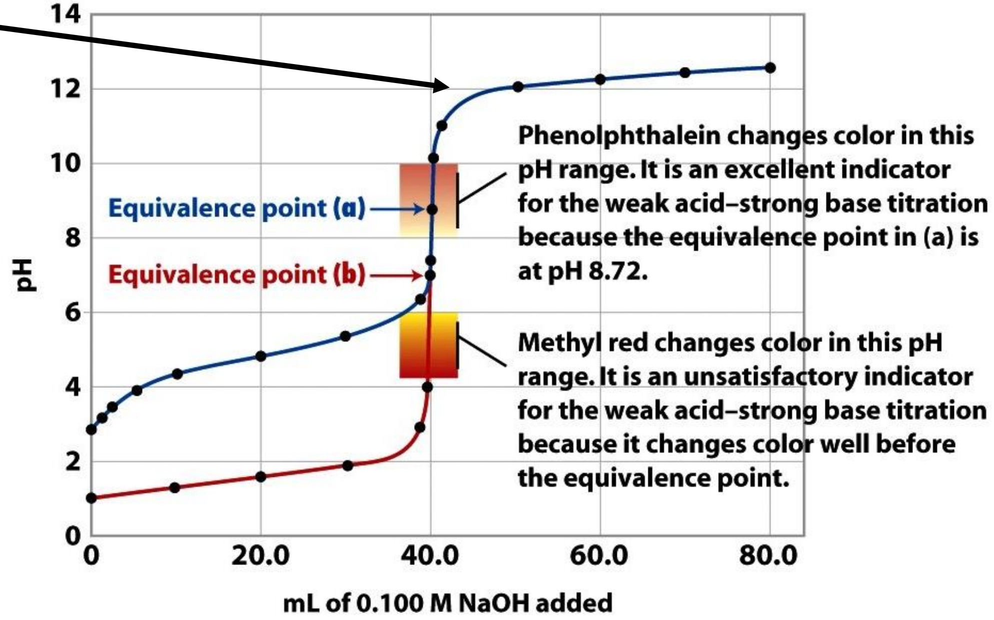
Figure 15-8 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Weak Acid-Strong Base Titrations

4. Beyond the Equivalence Point

Excess OH^{1-}

Notice that the strong and weak acid titration curves correspond *after* the equivalence point.



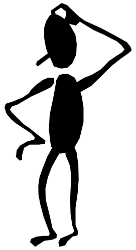
Phenolphthalein changes color in this pH range. It is an excellent indicator for the weak acid–strong base titration because the equivalence point in (a) is at pH 8.72.

Methyl red changes color in this pH range. It is an unsatisfactory indicator for the weak acid–strong base titration because it changes color well before the equivalence point.

Either phenolphthalein or methyl red can be used for the strong acid–strong base titration because the curve rises very steeply in the region of the equivalence point in (b) at pH 7.00.

Figure 15-8 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Which indicator(s) would you use for a titration of HNO_2 with KOH ?



Weak acid titrated with strong base.

At equivalence point, will have conjugate base of weak acid.

At equivalence point, pH > 7

Use cresol red or phenolphthalein = Salt KNO_2 is basic

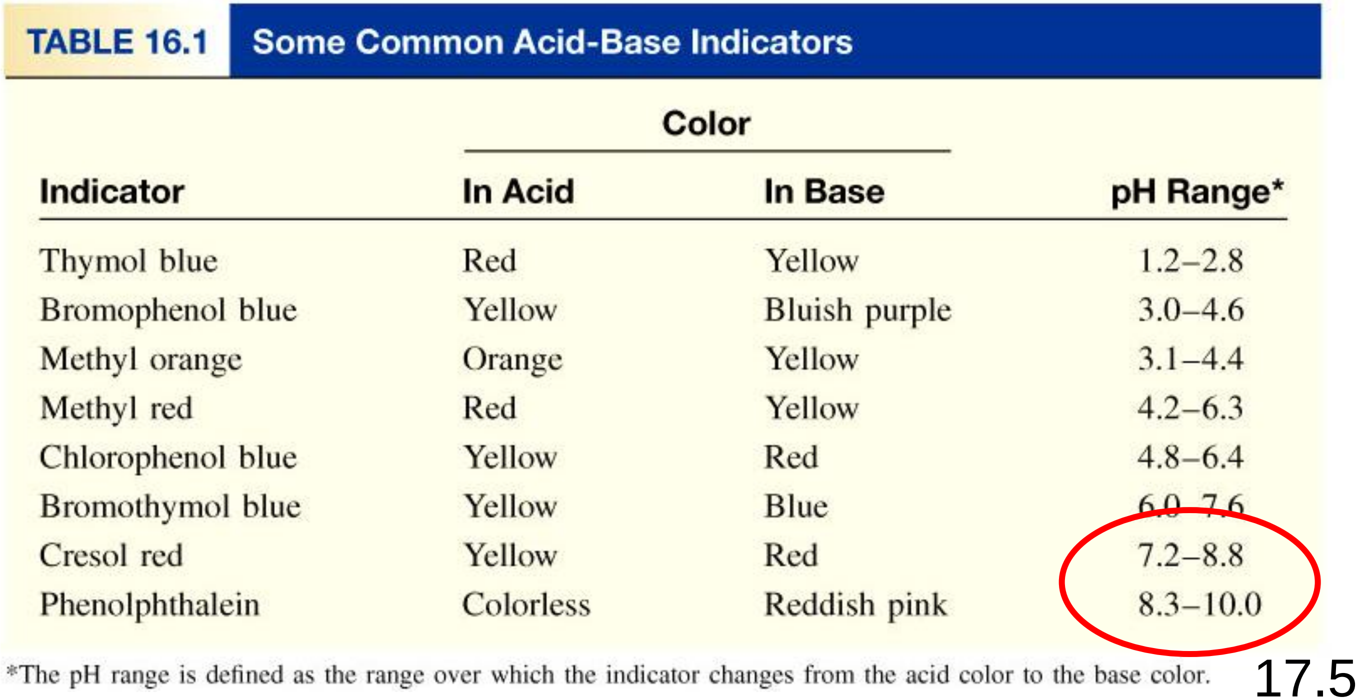


TABLE 16.1 **Some Common Acid-Base Indicators**

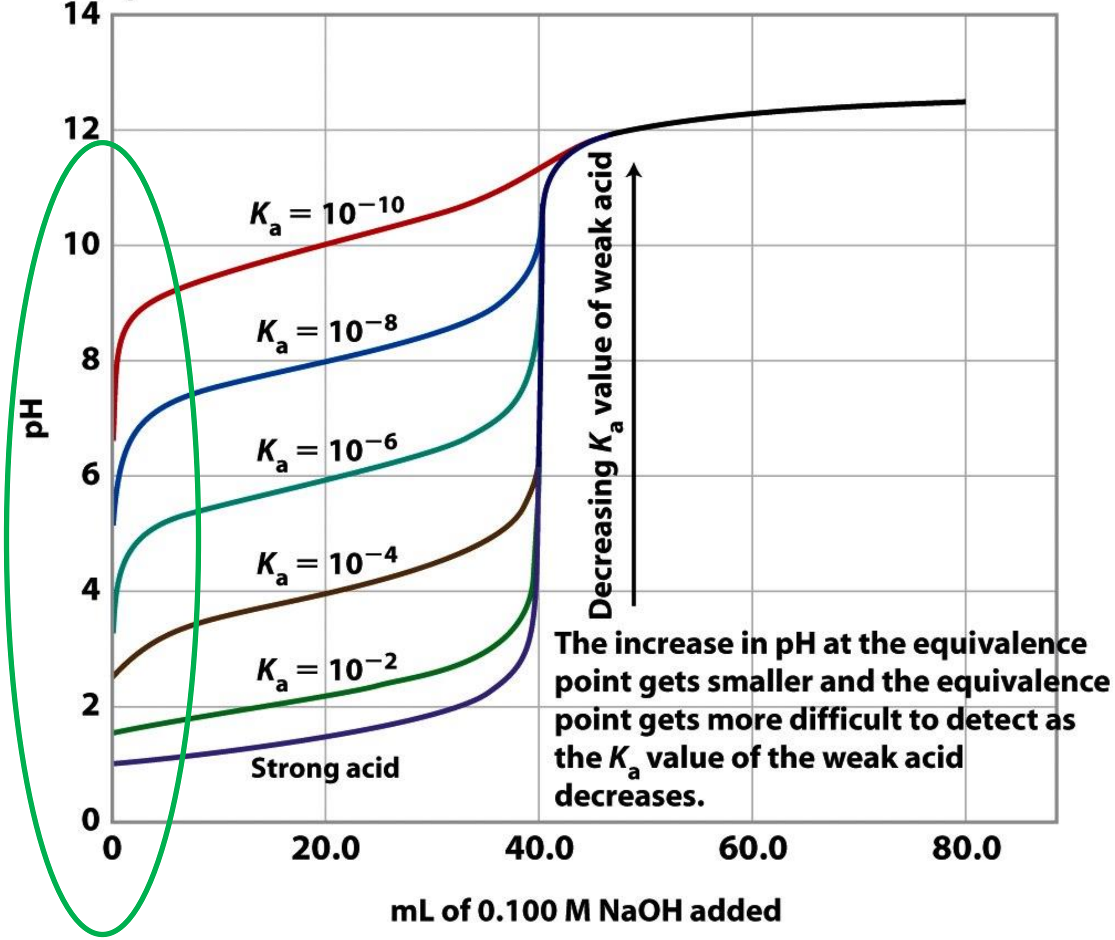
	Color		
Indicator	**In Acid**	**In Base**	**pH Range***
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8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

Weak Acid-Strong Base Titrations

5 acids have the same equivalent

The curves shown are for titration of 40.0 mL of 0.100 M solutions of various weak acids with 0.100 M NaOH. In each case, the equivalence point comes after addition of 40.0 mL of the base.



The increase in pH at the equivalence point gets smaller and the equivalence point gets more difficult to detect as the K_a value of the weak acid decreases.

Figure 15-9 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

weak acid

↓

Strong acid

Titration of A Weak Polyprotic Acid

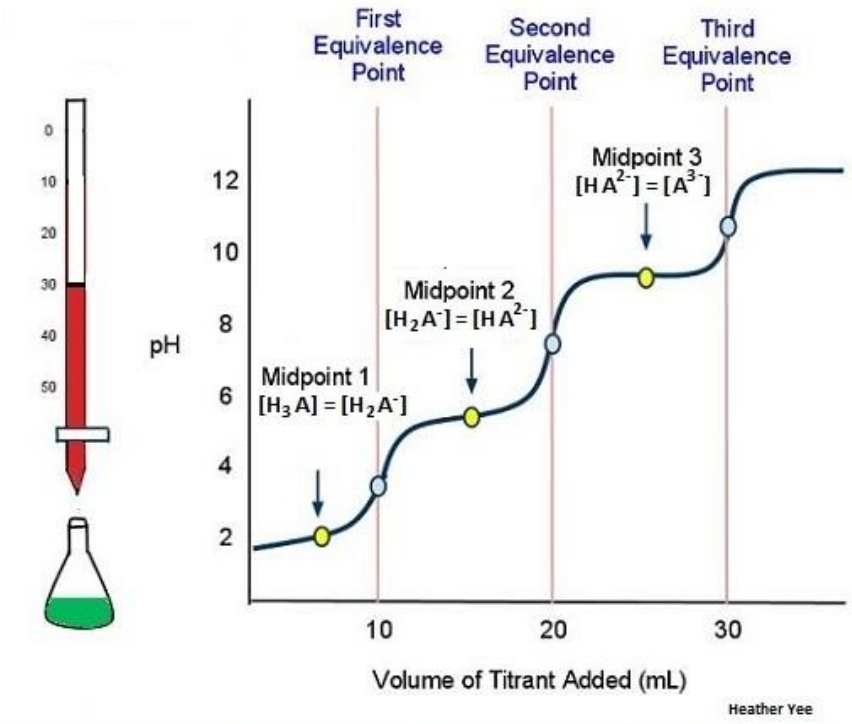


Figure 3.3 Titration of a Weak Polyprotic Acid. The final equivalence point is attained by adding another 10 mL, or a total of 30 mL, of the titrant to the weak polyprotic acid. Image created by Heather Yee.

Polyprotic acids and K_a values:

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ $K_{a1}=7.11\text{x}10^{-3}$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$ $K_{a2}=6.32\text{x}10^{-8}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$ $K_{a3}=4.5\text{x}10^{-13}$

$H_3PO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + PO_4^{3-}$ $K_{a1}K_{a2}K_{a3}$

$$H_3PO_4 + 3H_2O \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3\left[PO_4^{3-}\right]}{\left[H_3PO_4\right]} = 2.0x10^{-22}$$

1. pH before titration
2. pH before first equiv. point
3. pH at first equiv. pt.
4. pH between equiv. pts.
5. pH at second equiv. pt.
6. pH after second equiv. pt.
7. **more…**

Polyprotic Acid-Strong Base Titrations

Because K_{a1} and K_{a2} are separated by several powers of 10, the titration curve exhibits two well defined equivalence points, at pH 6.02 and pH 11.85, and two buffer regions, near pH 2.34 and pH 9.69.

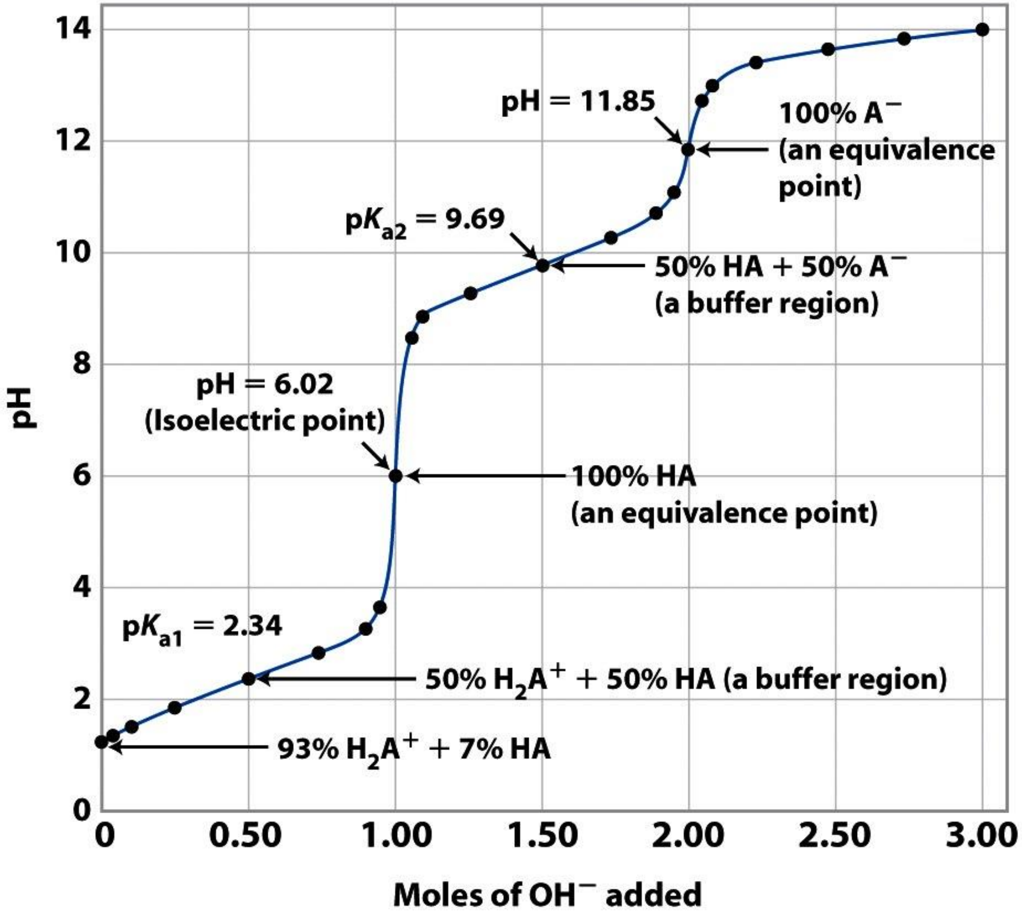


Figure 15-11 Chemistry, 5/e

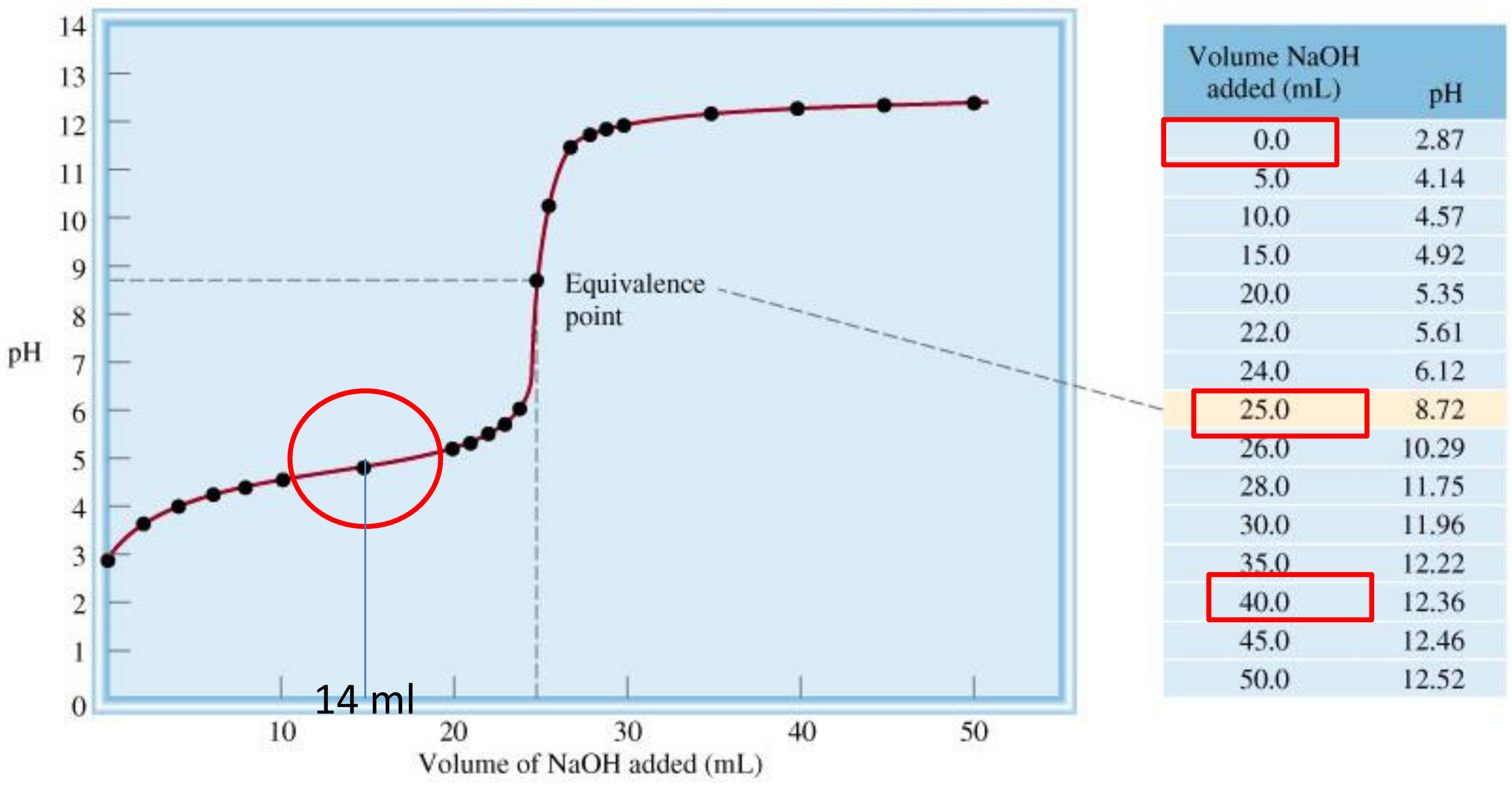
Weak Acid-Strong Base Titration Calculation

$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (l)$

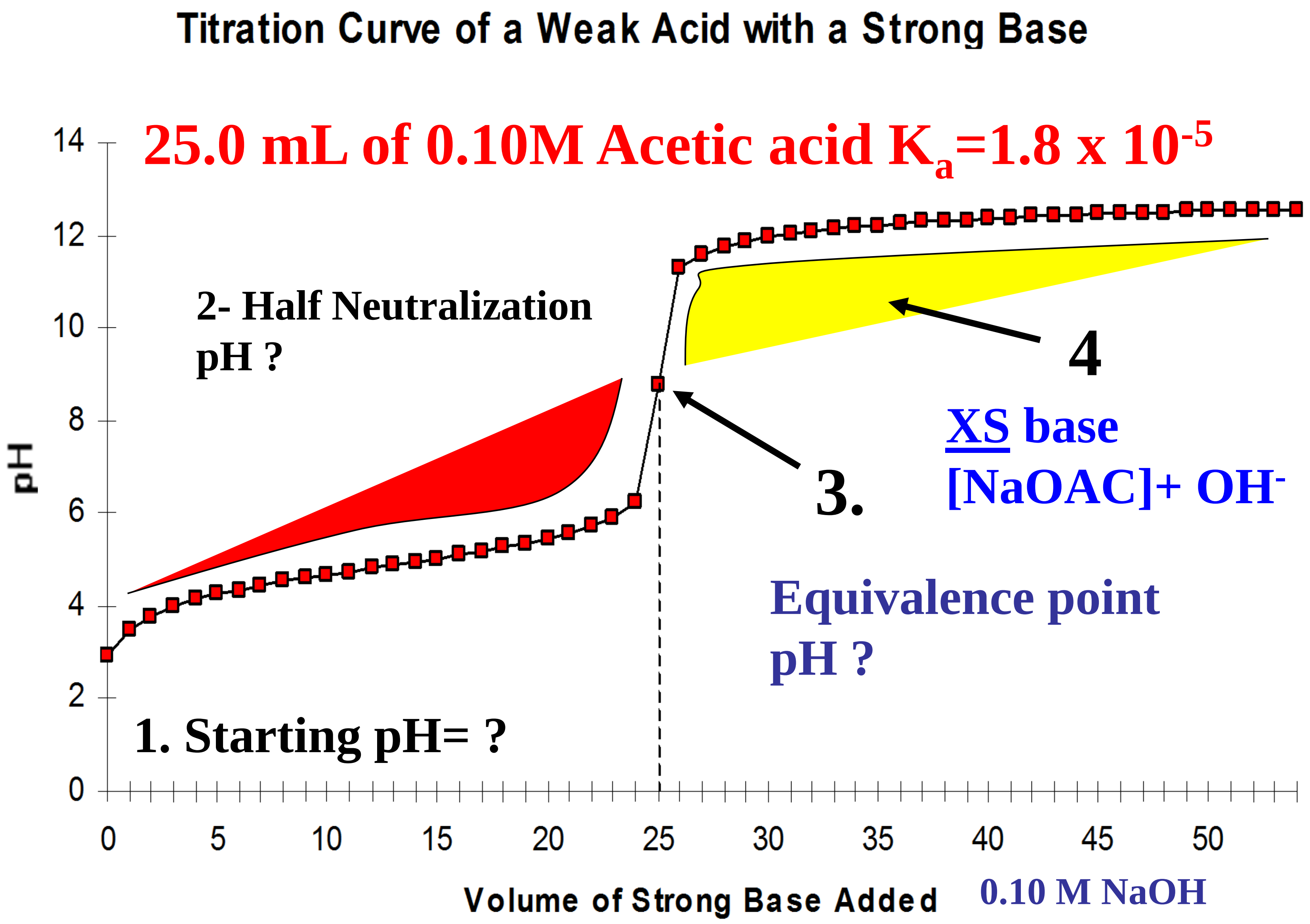
$CH_3COOH\ (aq) + OH^-\ (aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$

At equivalence point (pH > 7): why ?

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



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52



25.0 mL of 0.10M Acetic acid $K_a=1.8 \times 10^{-5}$

2- Half Neutralization
pH ?

4

XS base
[NaOAC]+ OH^-

3.

Equivalence point
pH ?

1. Starting pH= ?

0.10 M NaOH

Example 16.7 Weak Acid–Strong Base Titration pH Curve

A 40.0 mL sample of 0.100 M HNO_2 is titrated with 0.200 M KOH. Calculate:

- **a.** the volume required to reach the equivalence point
- **b.** the pH after adding 5.00 mL of KOH
- **c.** the pH at one-half the equivalence point

Solution

a. The equivalence point occurs when the amount (in moles) of added base equals the amount (in moles) of acid initially in the solution. Begin by calculating the amount (in moles) of acid initially in the solution. The amount (in moles) of KOH that must be added is equal to the amount of the weak acid.

$$\begin{aligned} \text{mol } HNO_2 &= 0.0400\ \cancel{\text{L}} \times \frac{0.100\ \text{mol}}{\cancel{\text{L}}} \\ &= 4.00 \times 10^{-3}\ \text{mol} \\ \text{mol KOH required} &= 4.00 \times 10^{-3}\ \text{mol} \end{aligned}$$

Calculate the volume of KOH required from the number of moles of KOH and the molarity.

$$\begin{aligned} \text{volume KOH solution} &= 4.00 \times 10^{-3}\ \cancel{\text{mol}} \times \frac{1\ \text{L}}{0.200\ \cancel{\text{mol}}} \\ &= 0.0200\ \text{L KOH solution} \\ &= 20.0\ \text{mL KOH solution} \end{aligned}$$

Example 16.7 Weak Acid–Strong Base Titration pH Curve

Continued

b. Use the concentration of the KOH solution to calculate the amount (in moles) of OH^- in 5.00 mL of the solution.

$$\begin{aligned} \text{mol } OH^- &= 5.00 \times 10^{-3}\ \cancel{L} \times \frac{0.200\ \text{mol}}{1\ \cancel{L}} \\ &= 1.00 \times 10^{-3}\ \text{mol } OH^- \end{aligned}$$

Prepare a table showing the amounts of HNO_2 and NO_2^- before and after the addition of 5.00 mL KOH. The addition of the KOH stoichiometrically reduces the concentration of HNO_2 and increases the concentration of NO_2^-.

	$OH^-(aq)$ +	$HNO_2(aq)$ ⟶	$H_2O(l)$ +	$NO_2^-(aq)$
Before addition	≈0.00 mol	4.00×10^{-3} mol	—	0.00 mol
Addition	1.00×10^{-3} mol	—	—	—
After addition	≈0.00 mol	3.00×10^{-3} mol	—	1.00×10^{-3} mol

Since the solution now contains significant amounts of a weak acid and its conjugate base, use the Henderson–Hasselbalch equation and pK_a for HNO_2 (which is 3.34) to calculate the pH of the solution.

$$\begin{aligned} pH &= pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \\ &= 3.34 + \log\frac{1.00 \times 10^{-3}}{3.00 \times 10^{-3}} \\ &= 3.34 - 0.48 = 2.86 \end{aligned}$$

Example 16.7 Weak Acid–Strong Base Titration pH Curve

Continued

c. At one-half the equivalence point, the amount of added base is exactly one-half the initial amount of acid. The base converts exactly half of the HNO_2 into NO_2^-, resulting in equal amounts of the weak acid and its conjugate base. The pH is therefore equal to pK_a.

	$OH^-(aq)$	+ $HNO_2(aq)$	$\longrightarrow$ $H_2O(l)$	+ $NO_2^-(aq)$
Before addition	≈0.00 mol	4.00×10^{-3} mol	—	0.00 mol
Addition	2.00×10^{-3} mol	—	—	—
After addition	≈0.00 mol	2.00×10^{-3} mol	—	2.00×10^{-3} mol

$$
\begin{aligned}
\text{pH} &= \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} \\
&= 3.34 + \log\frac{2.00 \times 10^{-3}}{2.00 \times 10^{-3}} \\
&= 3.34 + 0 = 3.34
\end{aligned}
$$

For Practice 16.7

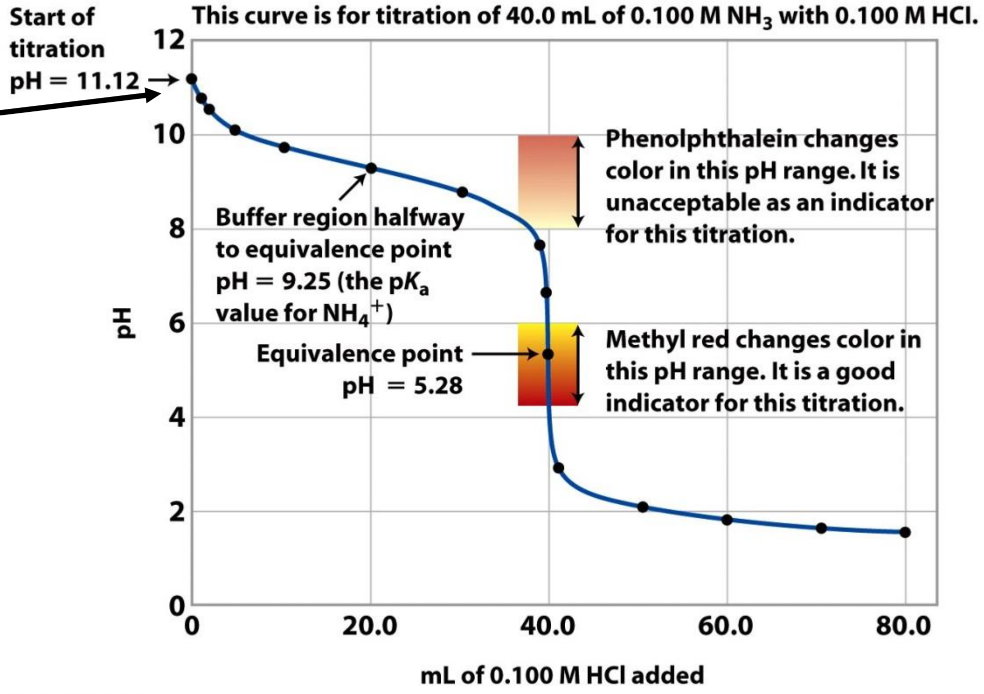
Determine the pH at the equivalence point for the titration of HNO_2 and KOH in Example 16.7.

Weak Base-Strong Acid Titrations

1. **Before Addition of Any HCl**

0.10 M NH_3 – $K_b = 1.8 \times 10^{-5}$ ($pK_a = 9.26$)

0.100 M NH_3


This curve is for titration of 40.0 mL of 0.100 M NH_3 with 0.100 M HCl.

Start of titration pH = 11.12

Buffer region halfway to equivalence point pH = 9.25 (the pK_a value for NH_4^+)

Equivalence point pH = 5.28

Phenolphthalein changes color in this pH range. It is unacceptable as an indicator for this titration.

Methyl red changes color in this pH range. It is a good indicator for this titration.

Figure 15-10 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Weak Base-Strong Acid Titrations

2. Before the Equivalence Point

$$NH_3(aq) + H_3O^{1+}(aq) \xrightarrow{100\%} NH_4^{1+}(aq) + H_2O(l)$$

Excess NH_3

Buffer region

$pH = pK_a + \log([NH_3]/[NH_4^+])$

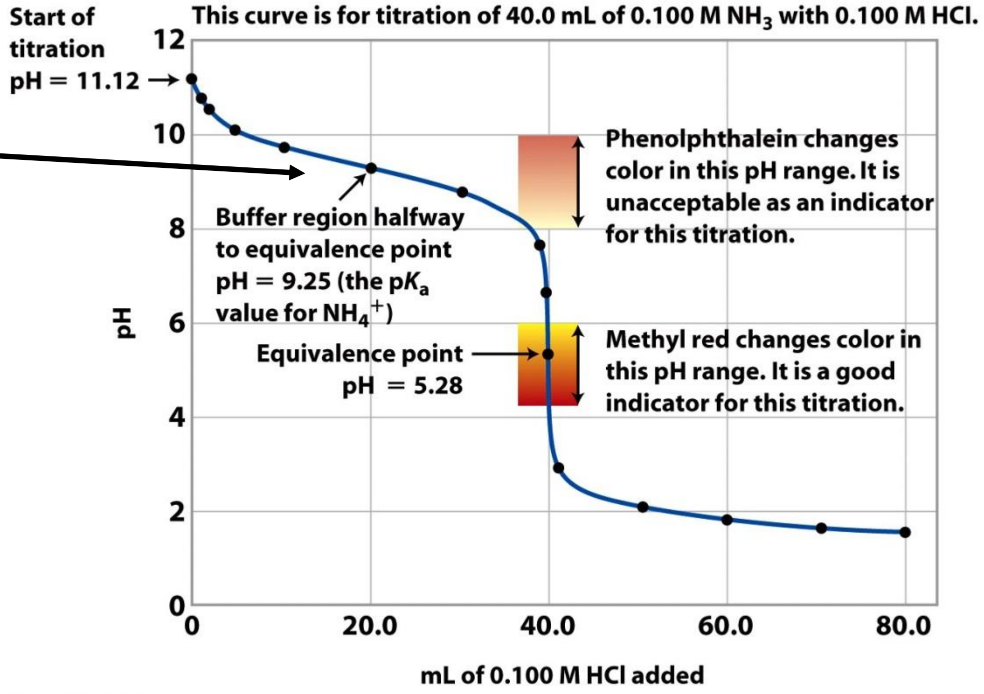

This curve is for titration of 40.0 mL of 0.100 M NH_3 with 0.100 M HCl.

Figure 15-10 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Weak Base-Strong Acid Titrations

3. At the Equivalence Point – NH4Cl salt (WB+SA), pH< 7

$$NH_4^{1+}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NH_3(aq)$$

pH < 7

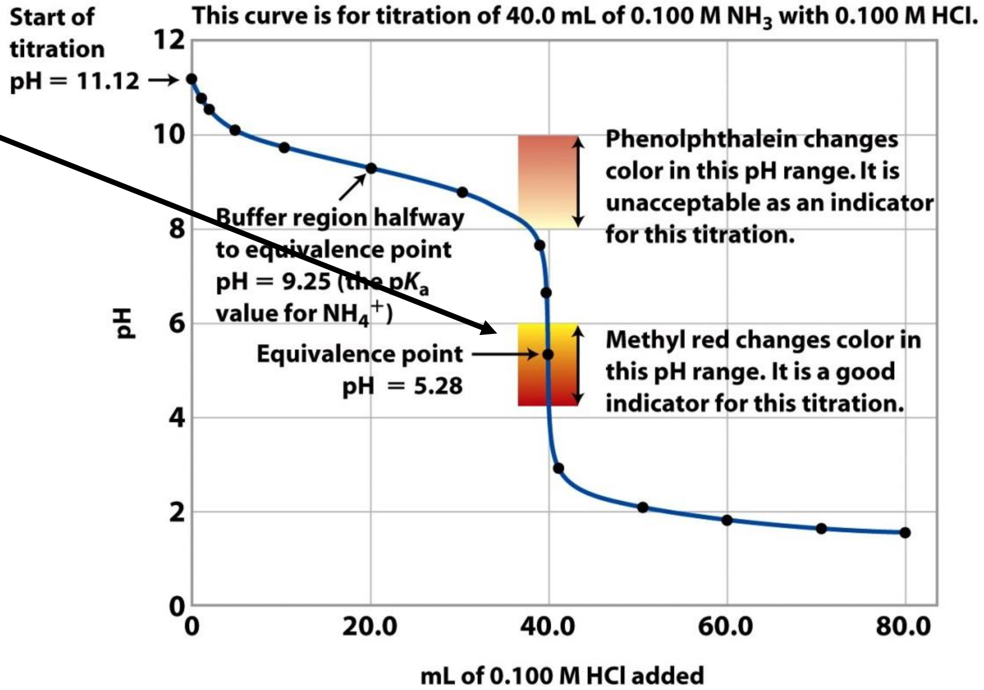


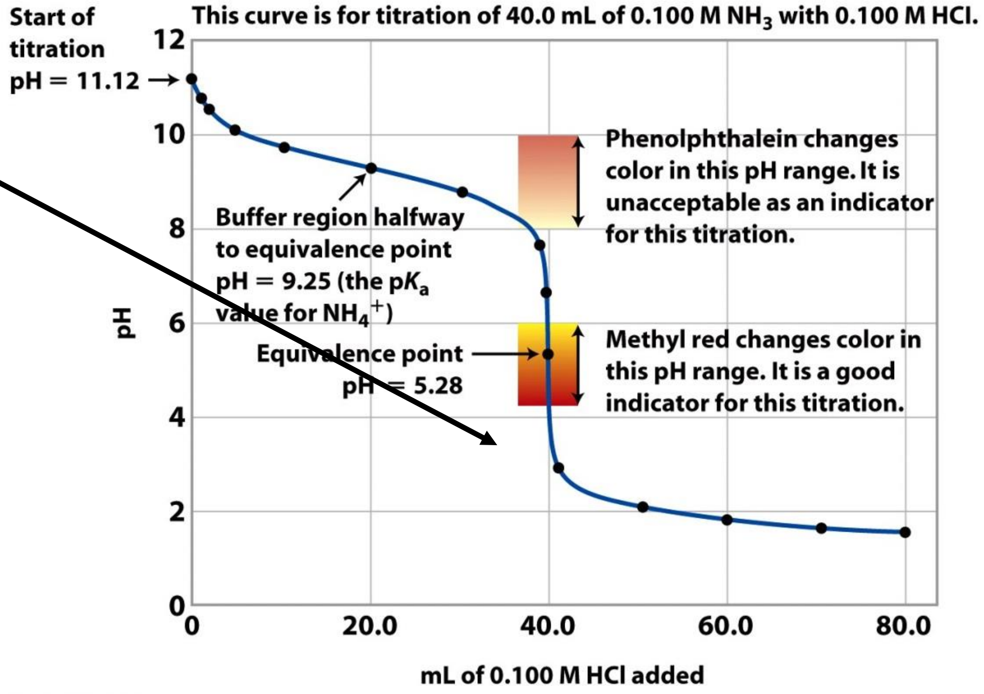
Figure 15-10 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.

Mole of acid = moles of OH⁻ added. Equivalence pt.

Weak Base-Strong Acid Titrations

4. Beyond the Equivalence Point

Excess H_3O^{1+}



This curve is for titration of 40.0 mL of 0.100 M NH_3 with 0.100 M HCl.

Start of titration pH = 11.12 →

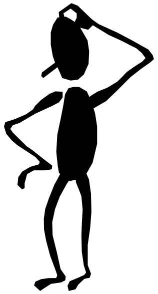
Buffer region halfway to equivalence point pH = 9.25 (the pK_a value for NH_4^+)

Equivalence point pH = 5.28

Phenolphthalein changes color in this pH range. It is unacceptable as an indicator for this titration.

Methyl red changes color in this pH range. It is a good indicator for this titration.

Figure 15-10 Chemistry, 5/e
© 2008 Pearson Prentice Hall, Inc.



Calculate the pH of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$$NH_4^+\ (aq) \rightleftharpoons H^+\ (aq) + NH_3\ (aq)$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} \qquad pK_a = 9.25 \qquad pH = 9.25 + \log\frac{[0.30]}{[0.36]} = 9.17$$

start (moles) 0.029 0.001 0.024

$$NH_4^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) + NH_3\ (aq)$$

end (moles) 0.028 0.0 0.025

final volume = 80.0 mL + 20.0 mL = 100 mL

$$[NH_4^+] = \frac{0.028}{0.10} \quad [NH_3] = \frac{0.025}{0.10} \qquad pH = 9.25 + \log\frac{[0.25]}{[0.28]} = 9.20$$

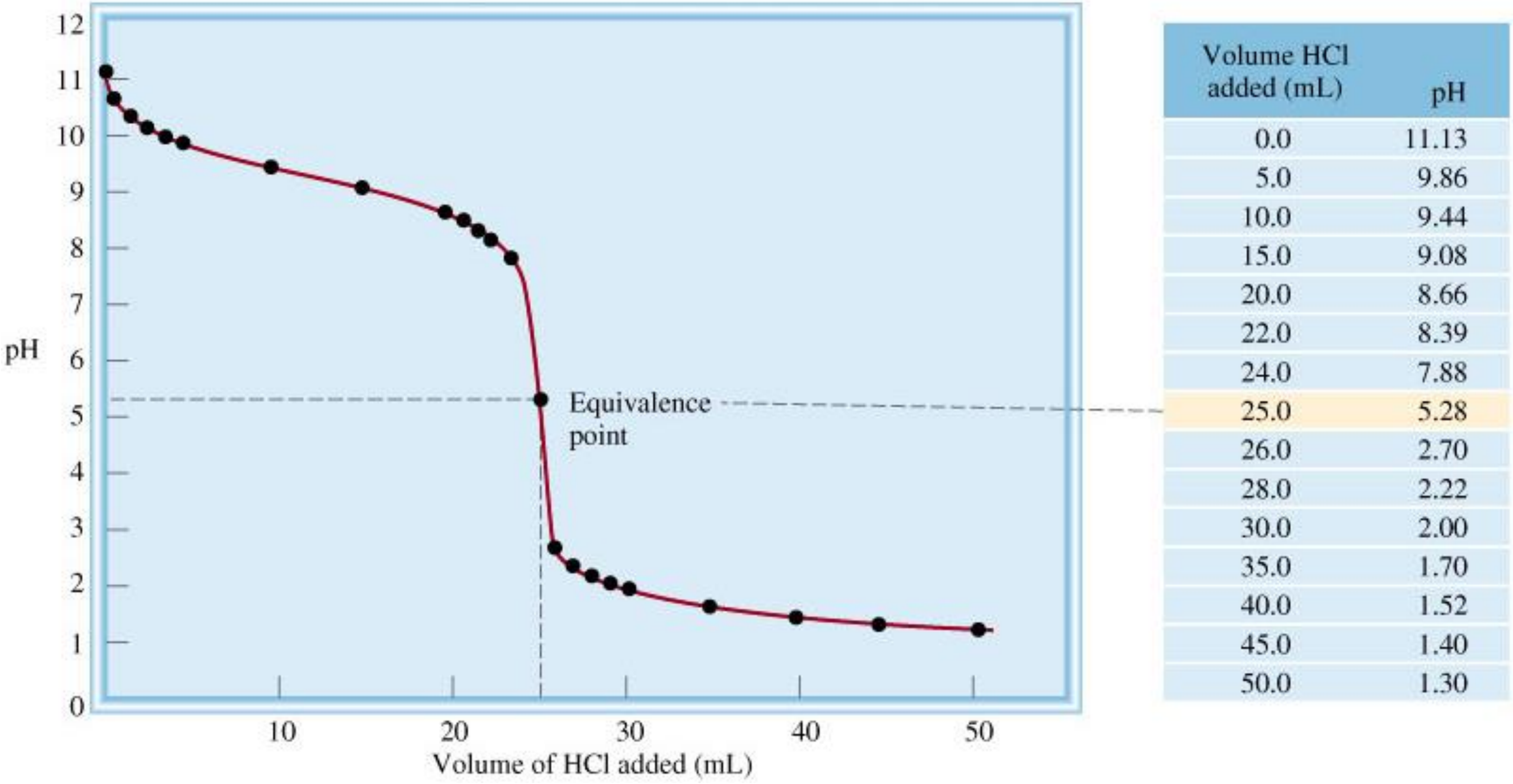
Strong Acid-Weak Base Titration Calculation

$HCl\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

$H^+\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

At equivalence point (pH < 7):

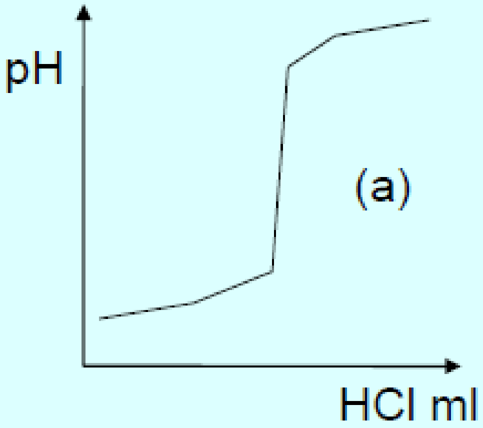
$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + H^+\ (aq)$

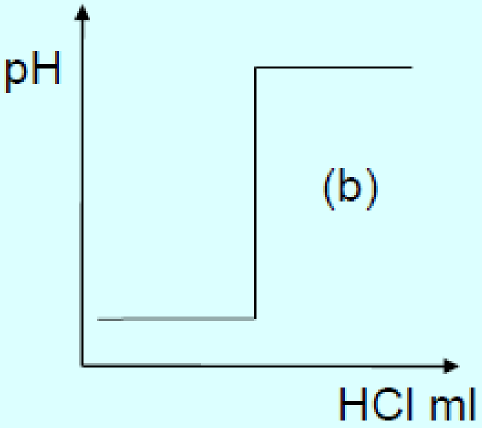


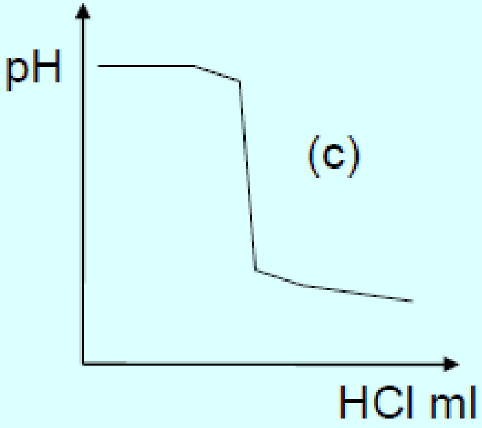
Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

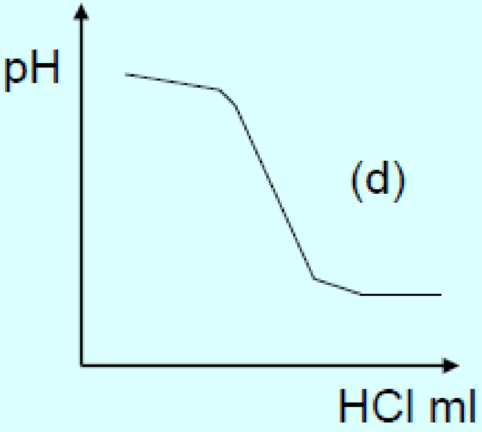
Question

Question: Which of the following titration curves properly shows the pH changes during the titration of NaOH by HCl?

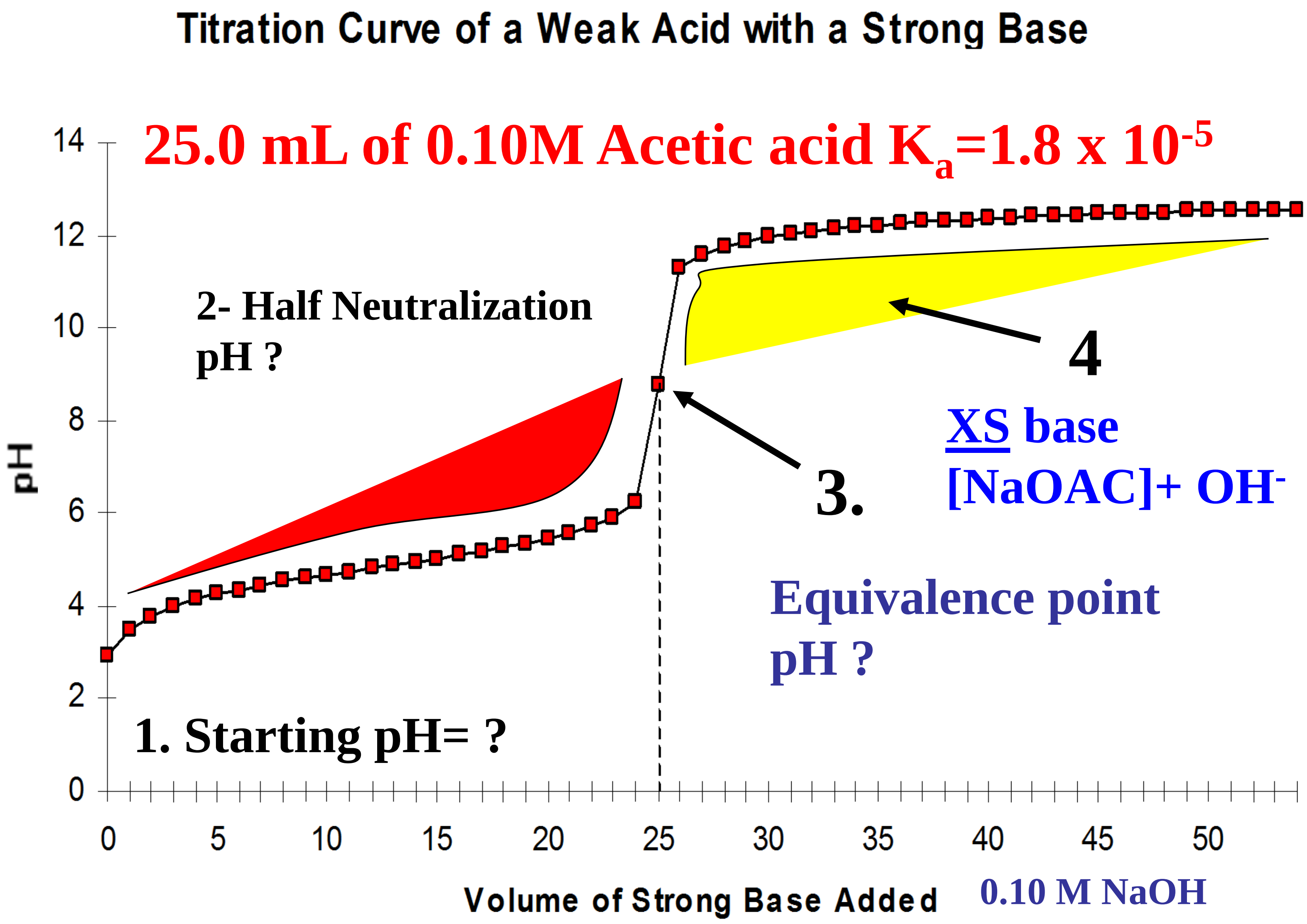








25.0 mL of 0.10M Acetic acid $K_a=1.8 \times 10^{-5}$



1. Starting pH= ?

2- Half Neutralization
pH ?

3.

Equivalence point
pH ?

4

<u>XS</u> base
[NaOAC]+ OH^-

0.10 M NaOH

Region 1 : Calculate the pH of 25.0 mL of 0.10M acetic acid (HOAc). The K_a of HOAc = 1.8 x 10^{-5}

Region 2- Start Titration

Problem: Calculate the pH of a solution that is prepared by combining 25.00mL of 0.10M acetic acid (HOAc) with 14.00mL of 0.080M NaOH. (Ka of HOAc = 1.8 x 10^{-5}).

Region 3. Equivalent Point – NaOAC salt , pH > 7

Region 3 problem: Calculate the pH at the equivalence point of a solution formed by the titration of 25.00mL of 0.10M acetic acid with 31.25mL of 0.080M NaOH K_a(HOAc)=1.8 x 10^{-5}.

Region 4 problem: Calculate the pH of a solution formed by the titration of 25.00mL of 0.10M acetic acid with 40.00mL of 0.080M NaOH. K_a(HOAc)=1.8 x 10^{-5}.

Region 1 : Calculate the pH of 25.0 mL of 0.10M acetic acid (HOAc). The K_a of HOAc = 1.8×10^{-5}

$HOAc \Leftrightarrow H^+ + OAC^-$

I	0.10	0	0
C	-x	+x	+x
E	0.10-x	x	x

$$K_a = \frac{[H+][OAc-]}{[HOAc]}$$

$$K_a = \frac{[x][x]}{0.10-x}$$

Small,drop, WHY?

$$K_a = \frac{x^2}{0.10}$$

$x = 0.00134 = [H^+]$

pH = -log 0.00134 =2.87

Region 2- Start Titration

Problem: Calculate the pH of a solution that is prepared by combining 25.00mL of 0.10M acetic acid (HOAc) with 14.00mL of 0.080M NaOH. (Ka of HOAc = 1.8 x 10^{-5}).

Region 2, we have : HOAC and NaOAC

HOAc + NaOH ⇔ H2O + NaOAC-

I	**2.5 mmole**	**0**	**0**	**0**
C	**-1.12mmole**	**+1.12mmole**	**+1.12mmole**	**+1.12mmole**
E	**1.38 mmole**			**+1.12mmole**

Problem: Calculate the pH of a solution that is prepared by combining 25.00mL of 0.10M acetic acid (HOAc) with 14.00mL of 0.080M NaOH. (Ka of HOAc = 1.8×10^{-5}).

1. initial M of Acid: $HOAc + OH^- \rightarrow H_2O + OAc^-$ 1:1 ratio

0.00138 mole/0.039L = 0.0354 M acid after RXN =INITIAL

2. initial M of OAC$^-$ anion from M of OH$^-$

0.00112 mole/0.039L = 0.0287 M OAc$^-$ after RXN =INITIAL**

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

	$[HOAc]$	$\Leftrightarrow$ $[H^+]$	$+ [OAc^-]$
I**	0.0354	0	0.0287
C	-x	+x	+x
E	0.0354-x	x	0.0287+x

$$1.8 \times 10^{-5} = \frac{[x][0.0287 + x]}{[0.0354 - x]}$$

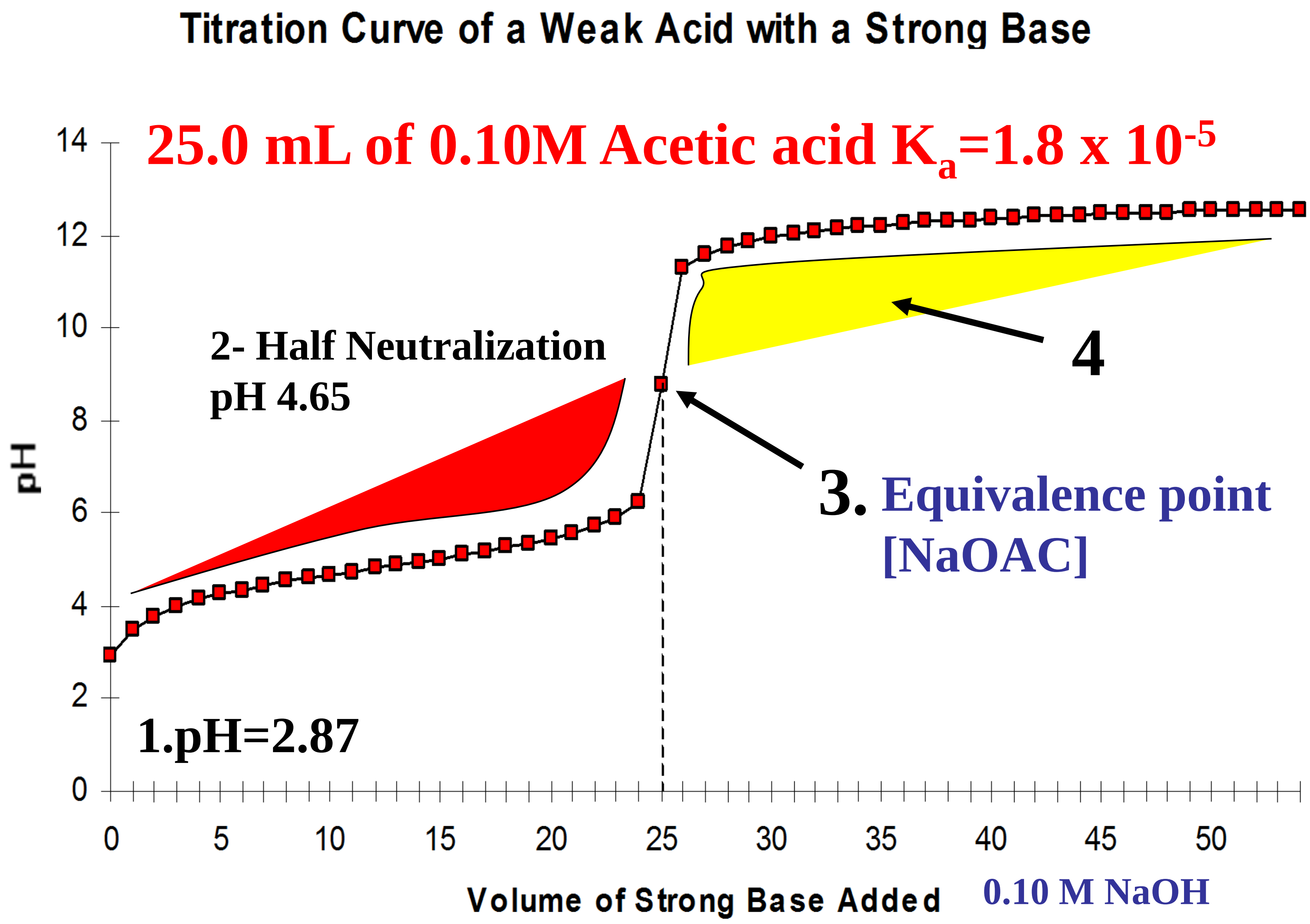
Can we drop these?

x = 0.0000222 =$[H^+]$

$$\boxed{pH = -\text{Log}\,[0.0000222] = 4.65}$$

Common Ion Effect – lower [H+] , higher pH

25.0 mL of 0.10M Acetic acid $K_a=1.8 \times 10^{-5}$



2- Half Neutralization
pH 4.65

3. **Equivalence point**
[NaOAC]

4

1.pH=2.87

0.10 M NaOH

Region 3. Equivalent Point.

Region 3 problem: Calculate the pH at the equivalence point of a solution formed by the titration of 25.00mL of 0.10M acetic acid with 31.25mL of 0.080M NaOH
K_a(HOAc)=1.8 x 10^{-5}.

Region 3, we have : NaOAC and it hydrolyzes

$$\mathbf{OAC^{-} + H2O \Leftrightarrow HOAc + OH^{-}}$$

I	**2.5 mmole**	**0**	**0**	**0**
C	**2.5 mmole-x**	**0**	**x**	**x**
E	**2.5 mmole-x**	**0**	**x**	**x**

Region 3 problem: Calculate the pH at the equivalence point of a solution formed by the titration of 25.00mL of 0.10M acetic acid with 31.25mL of 0.080M NaOH $K_a(\text{HOAc}) = 1.8 \times 10^{-5}$.

1. Find moles of Acid (which =‘s moles of base at Eq pt.)

$$\left.\frac{25.00\text{mL}}{\;}\right|\frac{0.10\text{mol HOAc}}{1000\text{mL}} = 0.0025\ \text{mol HOac}$$

2. Find mol of OH^-

$$\left.\frac{31.25\text{mL}}{\;}\right|\left.\frac{0.080\text{mol NaOH}}{1000\text{mL}}\right|\frac{1\text{mol}OH^-}{1\text{mol NaOH}} = 0.0025\ \text{mol}\ OH^-$$

3. Since the # of moles are the same, this is at the Eq. Pt. and therefore the initial moles of OAc^- ion = 0.0025 mol

moles of Acid = moles of base = 0.0025 = Eq. Pt.

New Volume = 0.05625L..and [OAc$^-$] = 0.0025/0.05625=0.0444M

Question: What equilibrium(ia) gives rise to the pH?

1. hydrolysis of the acetate anion:

$$OAc^- + H_2O \Leftrightarrow HOAc + OH^-$$

$$K_b = \frac{[OH^-][HOAc]}{[OAc^-]}$$

$$K_b = \frac{[x^2]}{[0.0444 - x]}$$

	[OAc$^-$]	[HOAc]	[OH$^-$]
I	0.0444	0	0
C	-x	+x	+x
E	0.0444-x	x	x

moles of Acid = moles of base = 0.0025 = Eq. Pt.

New Volume = 0.05625L...... and $[OAc^-]$ =0.0444M

Question: What equilibrium(ia) gives rise to the pH?

1. hydrolysis of the acetate anion:

$$OAc^- + H_2O \Leftrightarrow HOAc + OH^-$$

$$K_b = \frac{[OH^-][HOAc]}{[OAc^-]}$$

$$K_b = \frac{[x^2]}{[0.0444 - x]}$$

	OAc^-	HOAc	OH^-
I	0.0444	0	0
C	-x	+x	+x
E	0.0444-x	x	x

Can we drop this x?

How do we find K_b?

Also: $\underline{K_aK_b=K_w=1.0 \text{ x } 10^{-14}}$ @25°C so $\underline{K_b=}$ $\underline{5.56 \text{ x } 10^{-10}}$

moles of Acid = moles of base = 0.0025 = Eq. Pt.

New Volume = 0.05625L...... and $[OAc^-]$ =0.0444M

Question: What equilibrium(ia) gives rise to the pH?

1. hydrolysis of the acetate anion:

$$OAc^- + H_2O \Leftrightarrow HOAc + OH^-$$

$$K_b = \frac{[OH^-][HOAc]}{[OAc^-]}$$

	OAc^-	HOAc	OH^-
I	0.0444	0	0
C	-x	+x	+x
E	0.0444-x	x	x

$$5.56 \times 10^{-10} = \frac{[x^2]}{[0.0444 - x]}$$

$x = 4.97 \times 10^{-6} = [OH^-]$

pOH = 5.30

pH =14 - 5.30 = <u>8.70</u>

Region 4 problem: **Calculate the pH of a solution formed by the titration of 25.00mL of 0.10M acetic acid with 40.00mL of 0.080M NaOH.** **$K_a(\text{HOAc}) = 1.8 \times 10^{-5}$.**

1. Find moles of acid:

$$\left.\frac{25.00\text{mL}}{}\right|\frac{0.10\text{mol HOAc}}{1000\text{mL}} = 0.0025 \text{ mol HOAc}$$

2. Find moles of OH^-:

$$\left.\frac{40.00\text{mL}}{}\right|\frac{0.080\text{mol}OH^-}{1000\text{mL}} = 0.0032 \text{ mol } OH^-$$

3. Subtract to find XS:

0.0032 - 0.0025 = 0.0007 mole XS OH^-

4. Find OH^- concentration, pOH, and pH:

pOH = -Log[0.0007/0.06500] = 1.97 and pH = 12.03

Region 4 tips :

All the acid has been neutralized and XS base has been added

$$HA + OH^- \rightarrow H_2O + A^- + \underline{XS}\ OH^-$$

What is the dominating factor that controls the pH?

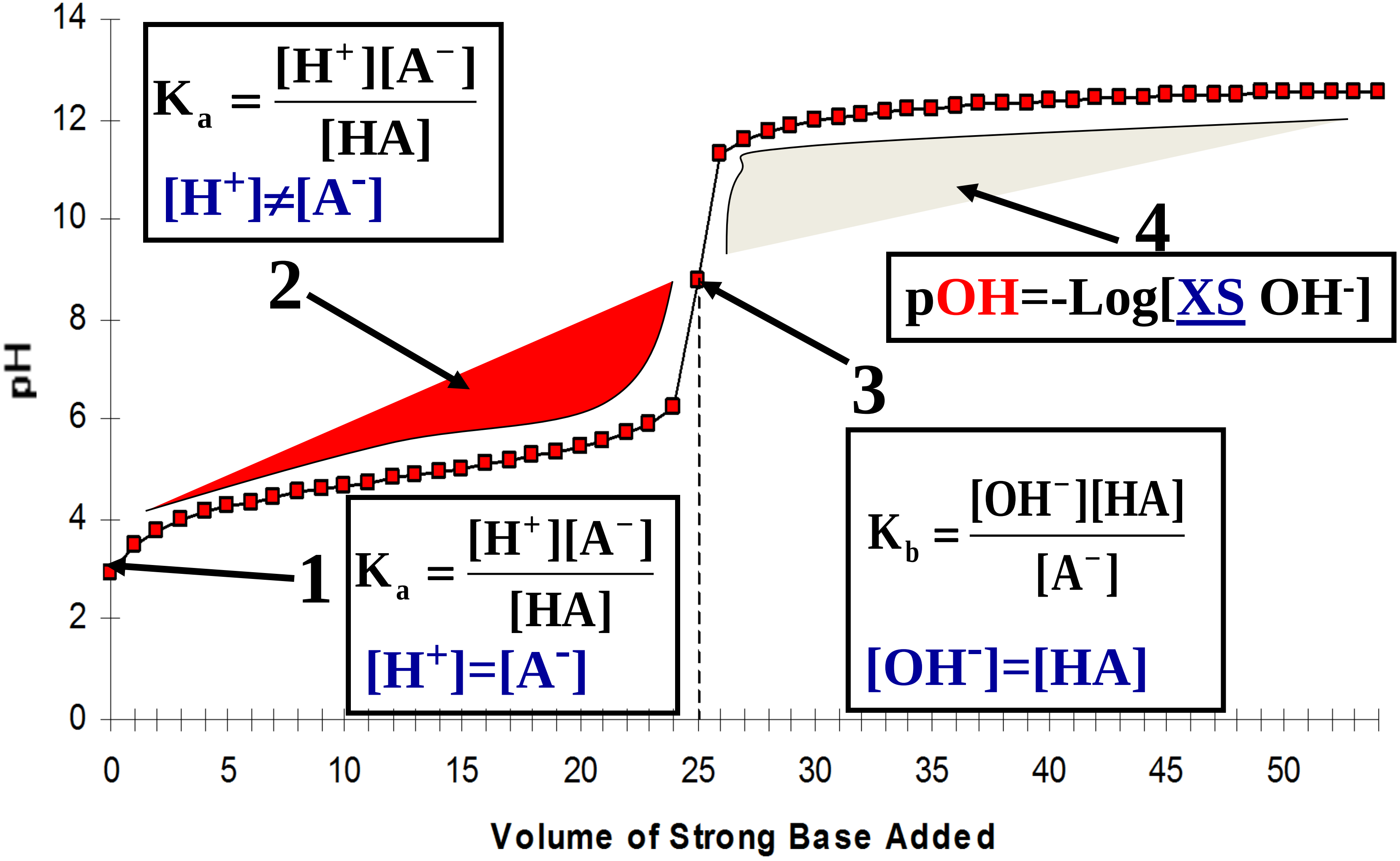
The XS strong base (OH^-)

Calculations:

Find moles of XS OH^- and then use the new volume to find $[OH^-]$ and then the pOH and pH.

Titration Curve of a Weak Acid with a Strong Base

Exam



$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$[H^+] \neq [A^-]$

$pOH = -Log[\underline{XS}\ OH^-]$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$[H^+] = [A^-]$

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

$[OH^-] = [HA]$