

**Reading for Today:** Sections 12.4-12.6 in 5<sup>th</sup> ed. (4<sup>th</sup> ed: 11.4-11.6)

**Reading Lecture #24:** Section K

**Topics:** Acid-Base Titrations

I. Titration of Strong Acids and Strong Bases

II. Titration of Weak Acids/Strong Bases & Strong Acids/Weak Bases

## ACID BASE TITRATIONS

An acid-base titration is the addition of a volume of base of known concentration to acid of unknown concentration (or addition of acid to base).

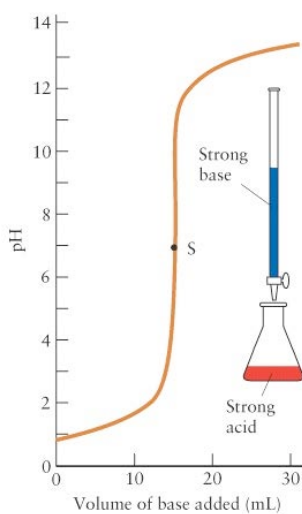
This technique can be used to determine the \_\_\_\_\_ of an acid or base.

### I. TITRATION OF STRONG ACIDS AND STRONG BASES

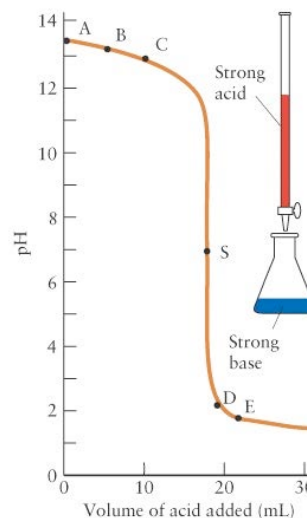
#### A. Shapes of Curves and Some Definitions

In a titration of a strong acid with a strong base, or a strong base with a strong acid, the pH changes slowly initially, changes rapidly through pH 7 at the equivalence point and then changes slowly again.

Titration curves:



Strong Acid titrated with Strong Base



Strong Based titrated with Strong Acid

Figure by MIT OpenCourseWare.

**Equivalence (stoichiometric, S) point** = *theoretical* volume at which moles of base (or acid) added equals moles of acid (or base) that was originally present.

**End point** = *experimentally* measured volume at which the indicator changes color.

Endpoint should \_\_\_\_\_ equivalence point.

**pH indicators** are weak acids or weak bases that have different colors based on different chemical structures in acidic or basic environments. Anthocyanins are examples of natural acid-base indicators.

## B. Calculating Points on a pH Curve for a Strong/Strong Acid-Base Titration

Example: a strong base (0.250 M NaOH) is titrated with a strong acid (0.340 M HCl)

1. Calculating the pH before the equivalence point when 5.00 mL of 0.340 M HCl (aq) is added to 25.00 mL of 0.250 M NaOH (aq)

a). Calculate moles of OH<sup>-</sup> present.  
(Base is strong so moles of NaOH added \_\_\_\_\_ moles of OH<sup>-</sup> formed.)

$$0.02500 \text{ L} \times 0.250 \text{ mol/L} = 6.25 \times 10^{-3} \text{ moles of OH}^- \text{ present}$$

b). Calculate moles of H<sub>3</sub>O<sup>+</sup> supplied by titrant.  
(Acid is strong so moles HCl added \_\_\_\_\_ moles of H<sub>3</sub>O<sup>+</sup> formed.)

$$0.00500 \text{ L} \times 0.340 \text{ mol/L} = 1.70 \times 10^{-3} \text{ moles}$$

c). Find the moles of OH<sup>-</sup> remaining after the reaction with H<sub>3</sub>O<sup>+</sup> ions.  
because stoichiometry is 1:1

$$6.25 \times 10^{-3} \text{ moles} - 1.70 \times 10^{-3} \text{ moles} = 4.55 \times 10^{-3} \text{ mol of } \underline{\hspace{2cm}} \text{ left}$$

(Since all the moles of strong acid are gone, from this point on, it is a **strong base in water** problem, and pH can be calculated from pOH, and pOH can be calculated from [OH<sup>-</sup>])

d). Calculate molarity of OH<sup>-</sup>

$$4.55 \times 10^{-3} \text{ mol} / 0.03000 \text{ L} = 0.152 \text{ mol/L} \text{ (recall volume is now 5.00 mL + 25.00 mL)}$$

e). Calculate pH

$$\text{pOH} = -\log 0.152 = 0.818 \qquad \text{pH} = 14.00 - 0.818 =$$

2. Calculating the volume of HCl needed to reach the equivalence point.

Initially  $6.25 \times 10^{-3}$  mol of OH<sup>-</sup> were present. At the equivalence point, \_\_\_\_\_ mol of HCl will have been added (1:1 stoichiometry)

$$6.25 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.340 \text{ mol}} = 0.0184 \text{ L}$$

3. What is the pH at the equivalence point?

4. Calculate the pH after 1.00 mL of HCl has been added after equivalence point has been reached. Note: this is a **strong acid in water** problem.

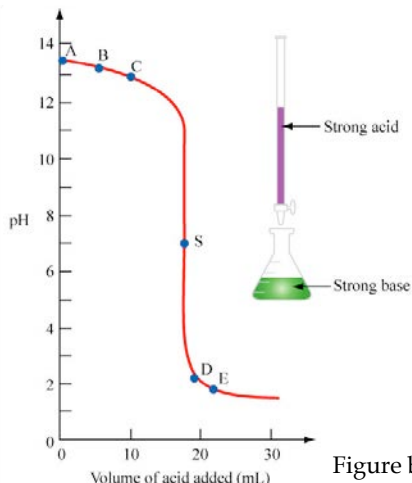
a). Find moles of H<sub>3</sub>O<sup>+</sup> formed due to the 1.00 mL addition of HCl  
(H<sub>3</sub>O<sup>+</sup> formed = amount of HCl added, since strong acid)

$$0.340 \text{ mol/L} \times (0.00100 \text{ L}) = 3.40 \times 10^{-4} \text{ mol of H}_3\text{O}^+$$

b). Calculate molarity of H<sub>3</sub>O<sup>+</sup>

c). Calculate pH.  $\text{pH} = -\log (7.66 \times 10^{-3}) = 2.116$

### C. Plotting the Calculated Numbers:



Point B: 5.00 mL of strong acid added; pH =

Point S: \_\_\_\_\_ of strong acid added; pH =

Point D: 1.00 mL of strong acid beyond S; pH =

Figure by MIT OpenCourseWare.

## II. TITRATIONS OF WEAK ACID/STRONG BASE & WEAK BASE/STRONG ACID

### A. Shapes of Curves and Some Definitions

In a titration of a weak acid / base with a strong base / acid, the pH changes slowly initially, then reaches a flat part of the curve (the buffering region), and then starts to change again, and changes rapidly through the equivalence point region, and then changes slowly again.

Curve for titration of weak acid with strong base:

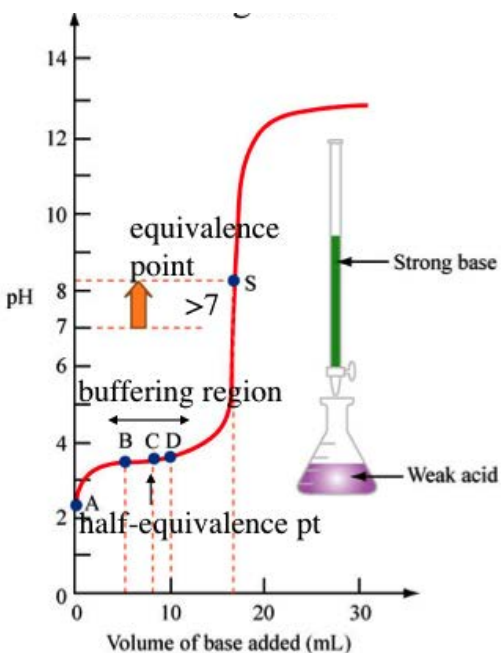
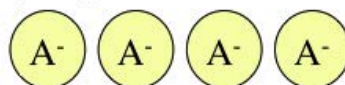


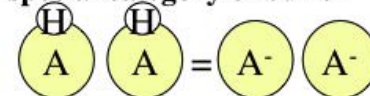
Figure by MIT OpenCourseWare.

$V > V_{eq}$  strong base in water

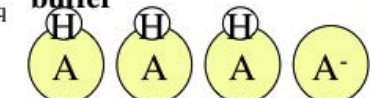
$V = V_{eq}$  (salt) conj. base of weak acid



$V = V_{half-eq}$  special category of buffer

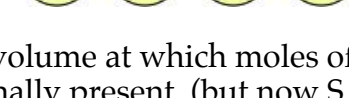
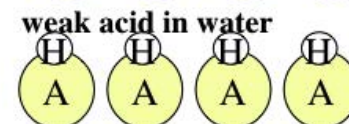


$0 < V < V_{eq}$  buffer



Start

$V = 0$



**Equivalence (stoichiometric, S) point** = theoretical volume at which moles of base (or acid) added equals moles of acid (or base) that was originally present. (but now S doesn't = 7)

**Buffering region:** flat part of curve where pH is constant

**Half-equivalence point:** = \_\_\_\_\_ the volume and \_\_\_\_\_ the number of moles needed to reach the equivalence point

**Curve for titration of weak base with strong acid:**

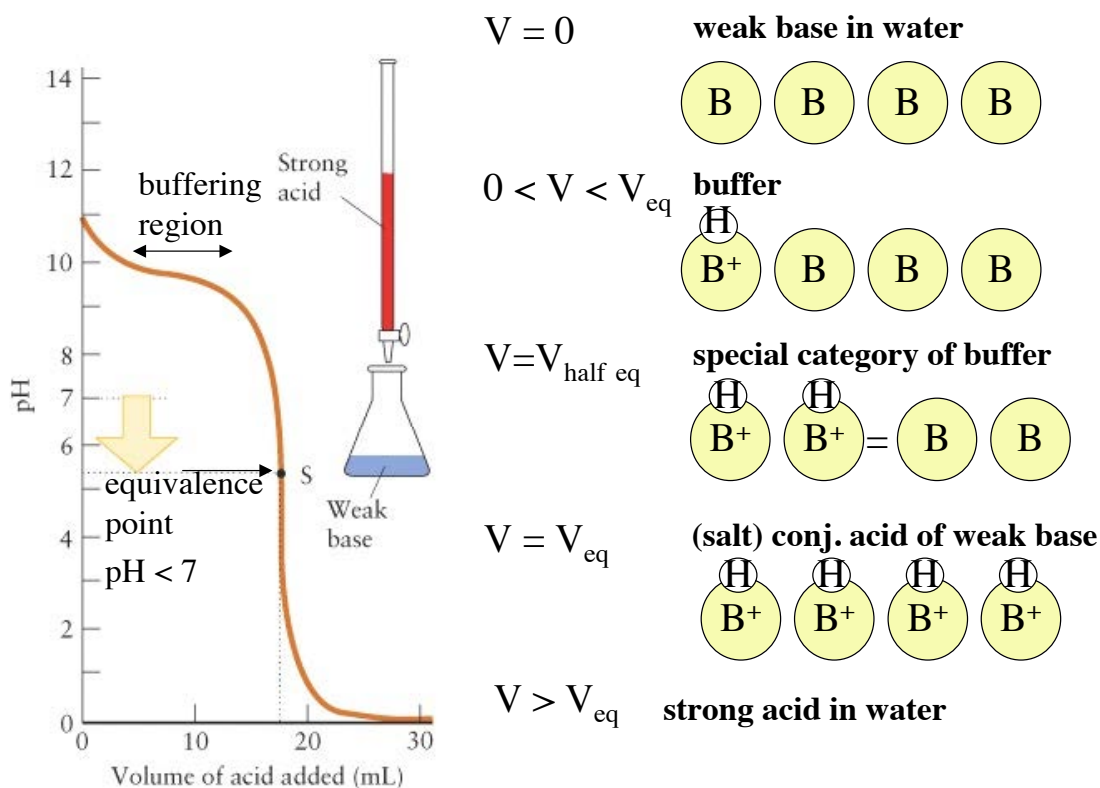


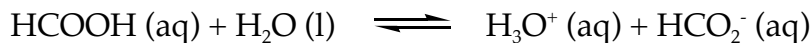
Figure by MIT OpenCourseWare.

**B. Calculating Points on a pH Curve for Weak Acid and Strong Bases**

**Example:** 25.0 mL of 0.10 M HCOOH with 0.15 M NaOH ( $K_a = 1.77 \times 10^{-4}$  for HCOOH)

1. Volume = 0 mL of NaOH added (Point A on plot on page 5)

Before any NaOH is added, the problem is that of an ionization of a weak acid in water.



	HCOOH (aq)	H <sub>3</sub> O <sup>+</sup> (aq)	+ HCO <sub>2</sub> <sup>-</sup> (aq)
initial molarity	0.10 M	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.10-x	x	x

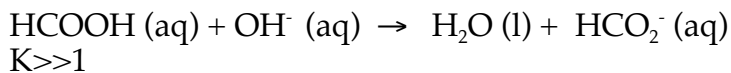
$$K_a = 1.77 \times 10^{-4} = \frac{(x)^2}{(0.10-x)} \approx \frac{(x)^2}{0.10}$$

$$x = 0.00421 \text{ (check } 0.00421 \text{ is } 4.2\% \text{ of } 0.10 \text{) okay}$$

$$\text{pH} = -\log [0.00421] = 2.38 \text{ ( ___ sig. fig. after decimal) (Point A on plot on next page)}$$

2.  $0 < V < V_{eq}$  (Points B-D on plot)  
 In this range, the acid has been partly ionized by the strong base (buffering region).

Calculate the pH of the solution resulting from the addition of 5.0 mL of 0.15 M NaOH (Point B)  
 Because OH<sup>-</sup> is a strong base, it reacts almost completely with HCOOH.



Initial Moles

For HCOOH,  $(25.0 \times 10^{-3} \text{ L})(0.10 \text{ M}) = 2.5 \times 10^{-3}$  moles

For OH<sup>-</sup>,  $(5.0 \times 10^{-3} \text{ L})(0.15 \text{ M}) = 0.75 \times 10^{-3}$  moles

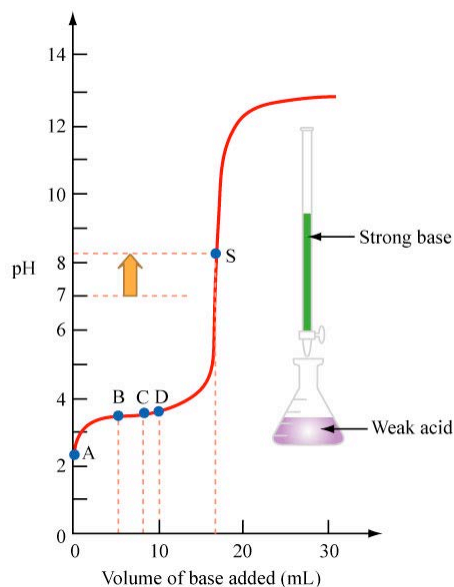


Figure by MIT OpenCourseWare.

Moles after Reaction

$2.5 \times 10^{-3}$  moles -  $0.75 \times 10^{-3}$  moles = \_\_\_\_\_ moles of HCOOH left

$0.75 \times 10^{-3}$  moles OH<sup>-</sup> produces \_\_\_\_\_ moles of HCO<sub>2</sub><sup>-</sup>

Molarity

$1.75 \times 10^{-3}$  moles of HCOOH /  $(0.0250 + 0.0050 \text{ L}) = 0.0583 \text{ M HCOOH}$

$0.75 \times 10^{-3}$  moles of HCO<sub>2</sub><sup>-</sup> /  $(0.0250 + 0.0050 \text{ L}) = 0.0250 \text{ M HCO}_2^-$

**Option 1 for calculating point B**

	HCOOH	H <sub>3</sub> O <sup>+</sup>	+ HCO <sub>2</sub> <sup>-</sup>
initial molarity	0.0583	0	0.0250
change in molarity	-x	+x	+x
equilibrium molarity	0.0583 - x	+x	0.0250 + x

$$K_a = 1.77 \times 10^{-4} = \frac{(0.0250 + x)(x)}{(0.0583 - x)} \quad \text{assume } x \text{ is small} \quad \approx \frac{0.0250x}{0.0583}$$

$$x = 4.13 \times 10^{-4}$$

Check assumption:  $4.13 \times 10^{-4}$  is 1.65% of 0.025 and is 0.7% of 0.0583 okay

$$\text{pH} = -\log [4.13 \times 10^{-4}] = 3.38$$

## Option 2 for calculating point B

$$\text{pH} \approx \text{pK}_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$\text{pH} \approx 3.75 - \log \left( \frac{[0.0583]}{[0.0250]} \right) = 3.75 - 0.368 = 3.38$$

Check Henderson-Hasselbalch assumption

for a pH of 3.38,  $[\text{H}_3\text{O}^+] = 4.2 \times 10^{-4}$

Check that  $4.2 \times 10^{-4}$  is  $< 5\%$  of 0.0250 (It is 1.7%. Okay)

If the 5% assumption isn't valid, than option 1 must be used, and

$K_a = 1.77 \times 10^{-4} = \frac{(0.0250 + x)(x)}{(0.0583 - x)}$  cannot be simplified. Must solve by quadratic equation.

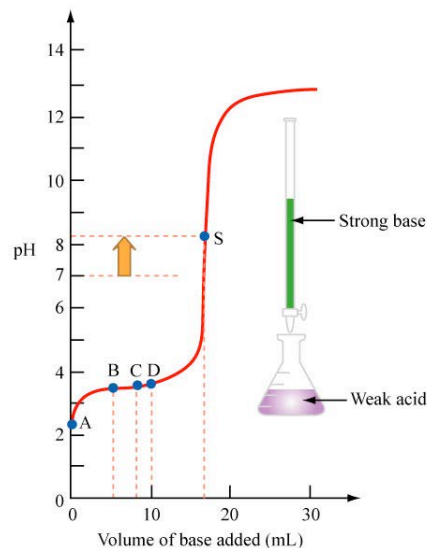


Figure by MIT OpenCourseWare.

Again, when the volume of NaOH added is between 0 and the equivalence volume  $V_{eq}$ , the problems are similar to buffer problems. This region of the titration curve is called the "buffering region."

## Half-equivalence point (Point C)

When the volume of NaOH added is equal to half the equivalence volume,  $[\text{HA}] = [\text{A}^-]$ .

$$\text{pH} \approx \text{pK}_a - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$\text{pH} \approx \text{pK}_a - \log (1)$$

$$\text{pH} \approx \text{pK}_a$$

$$\text{pH} = \text{pK}_a =$$

We will finish this titration next time, starting with Point S

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