

## Titrations: Stoichiometry in Action!

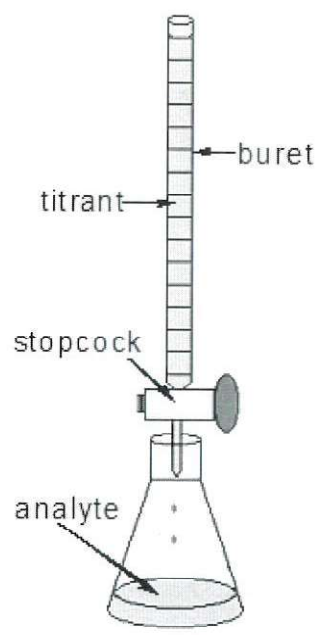


Figure 1: Titration Setup

A substance in a solution of Known concentration (the titrant, usually in a buret) is reacted with another substance in a solution of unknown concentration (the analyte, usually in a flask or beaker)

- **Equivalence point:** the point at which the moles of each reactant are *stoichiometrically equal* to each other in solution:  $\text{moles}(\text{H}^+) = \text{moles}(\text{OH}^-)$  because the acid and base have completely neutralized.
- **End point:** the point of the titration where an indicator changes color

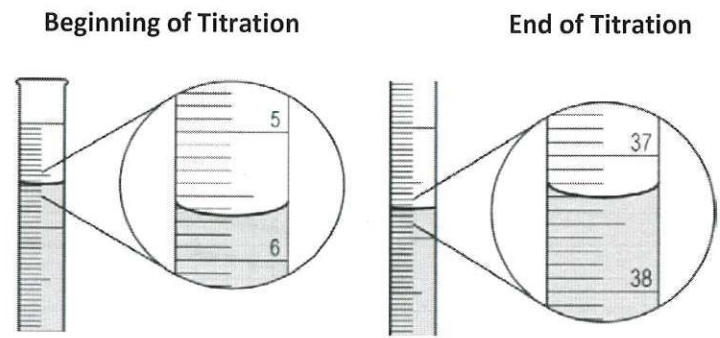
### How to Choose an Indicator

- Choose an indicator with pKa = pH at the equivalence point
- $K_a$  of the indicator  $\approx 1 \times 10^{-\text{pH @ eq pt}}$
- Indicator is a weak acid where HA and A<sup>-</sup> are different colors!
- If  $\text{pH} \leq \text{pKa}$  mostly HA (one color), if  $\text{pH} > \text{pKa}$  mostly A<sup>-</sup> (different color)

### Quick Reminder: How to Read a Buret

Burets, unlike most glassware, are read from the top down, not the bottom up!

*Example:* The image to the left shows a buret of NaOH before titration begins (leftmost) and at the end point (rightmost).



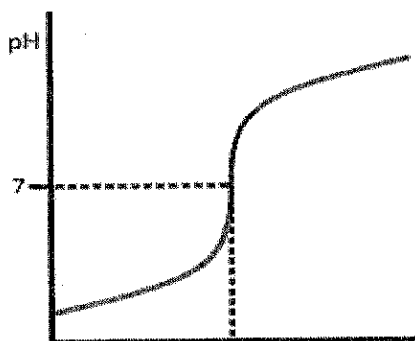
1. What volume of solution was initially present in the buret? 5.65 mL
2. What volume was present at the end point of the titration? 37.30 mL
3. How much NaOH solution was added to the flask?  
 $37.30 - 5.65 = \boxed{31.65 \text{ mL}}$

### Potential Titration Lab Errors

Error	Cause	Effect
1. Over-titration	Going <u>past</u> equivalence point by adding too much titrant	Calculated moles of titrant and thus calculated moles of analyte are too <u>large</u> .
2. Under-titration	Not reaching equivalence point by adding too little titrant	Calculated moles of titrant and thus calculated moles of analyte are too <u>small</u> .
3. Water added to titrant (buret)	<u>Buret</u> still wet from rinsing when it is filled with titrant	Actual concentration of titrant is lower than marked, so more volume was added, thus calculated moles of analyte are too <u>large</u> .
4. Water added to analyte (flask)	<u>Flask or beaker</u> is still wet from rinsing when analyte is added	Moles of analyte don't change, so <u>no effect</u> on calculated moles of analyte.

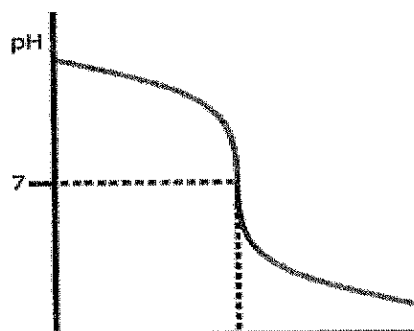
## Titration Types to Know, Part I: Strong/ Strong

Strong Acid Titrated w/ Strong Base



Titration curve of a strong acid (HCl) with a strong base (NaOH)

Strong Base Titrated w/ Strong Acid



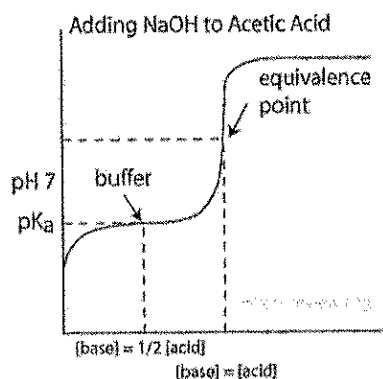
Titration curve of a strong base (NaOH) with a strong acid (HCl)

### Strong Acid + Strong Base (in either direction)

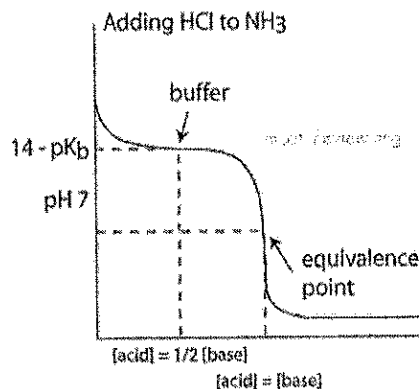
- At equivalence point,  $\text{pH} = 7$
- Net ionic will always be:  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
- Use  $M_a V_a = M_b V_b$  to calculate volume needed to reach equivalence point

## Titration Types to Know, Part II: Weak/ Strong

Weak Acid Titrated with Strong Base



Weak Base Titrated with Strong Acid



### pH at Equivalence point

- Weak acid + strong base:  $\text{pH} > 7$
- Weak base + strong acid:  $\text{pH} < 7$

1/2 Equivalence point (midpoint). A perfect buffer!  $[\text{HA}] = [\text{A}^-] !!$

- Weak acid + strong base:  $[\text{HA}] = [\text{A}^-]$ , thus  $[\text{H}_3\text{O}^+] = K_a$  and  $\text{pH} = \text{p}K_a$
- Weak base + strong acid:  $[\text{B}] = [\text{BH}^+]$ , thus  $[\text{OH}^-] = K_b$  and  $\text{pH} = 14 - \text{p}K_b = \text{p}K_a$  (of conj. acid)

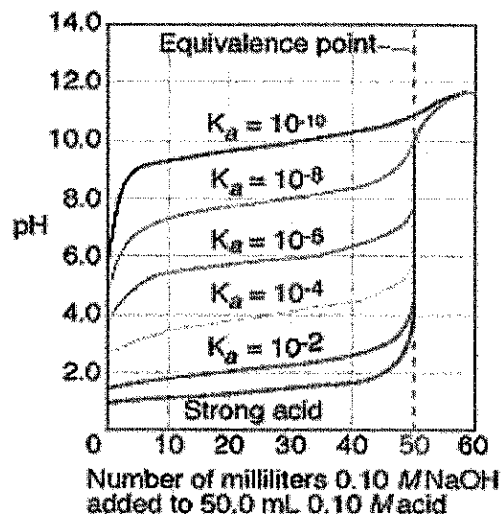
\*Note: We can still use  $M_a V_a = M_b V_b$  to calculate volume needed to reach equivalence point!

## How Increasing $K_a$ Affects the Titration Curve

Notice the effect of increasing the  $K_a$  value of the titrated acid on the titration curve in the image to the right.

Things to note:

1. The equivalence point *volume* does NOT change, regardless of the strength of the acid (always  $V_A M_A = V_B M_B$ ).
2. Equivalence point pH does change.
3. The initial steep increase (at the very beginning of the titration curve) decreases and ultimately disappears as the strength of the acid increases.

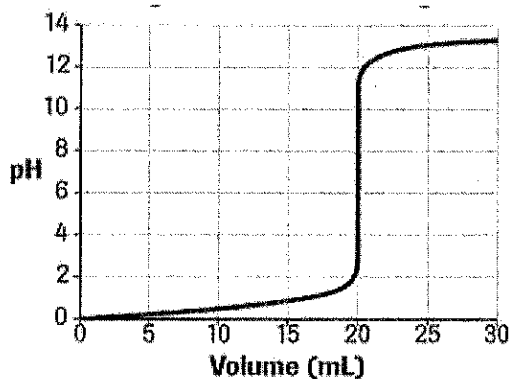


## How to Determine $pK_a/pK_b$ of Weak Acid or Base from Titration Data

1. Calculate location of  $1/2$ -equivalence point by dividing volume at equivalence point in half! (1.5)
2. Use titration curve to determine the pH at the half-equivalence point.
  - a. Analyte a weak acid?  $pH = pK_a$ ,  $K_a = 1 \times 10^{-pH}$
  - b. Analyte a weak base?  $pH = pK_a$  (of  $BH^+$ ), so  $pK_b = 14 - pH$ ,  $K_b = 1 \times 10^{-(14-pH)}$

Let's Practice! Assume the acid and base solutions for each of the following graphs are equimolar.

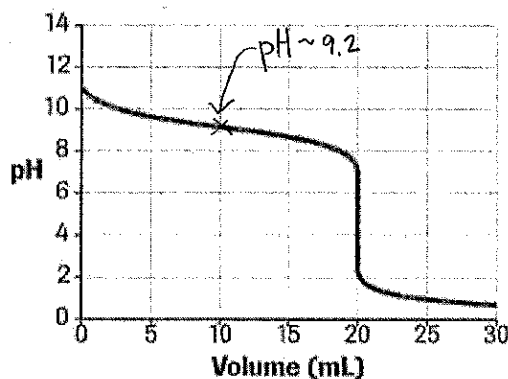
Graph 1



- 1) What type of titration? SA w/ SB
- 2) At the equivalence point,  $pH \approx$  7
- 3) If possible, determine the  $pK_a$  or  $pK_b$  of the analyte (and identify if your value is  $pK_a$  or  $pK_b$ ).

n/a

Graph 2

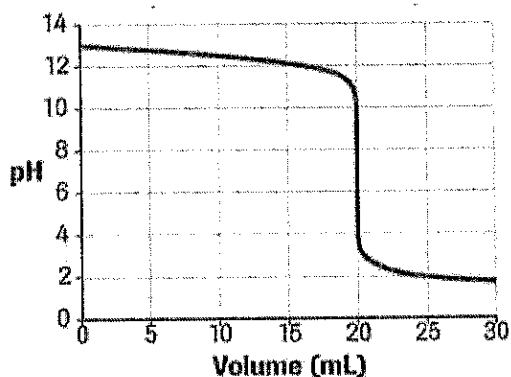


- 1) What type of titration? WB w/ SA
- 2) At the equivalence point,  $pH \approx$  5
- 3) If possible, determine the  $pK_a$  or  $pK_b$  of the analyte (and identify if your value is  $pK_a$  or  $pK_b$ ).

$$pK_b = 14 - 9.2 = 4.8$$

$$K_b = 1 \times 10^{-4.8}$$

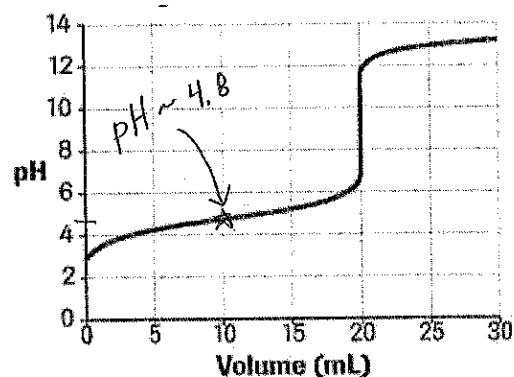
Graph 3



- 1) What type of titration? SB w/ SA
- 2) At the equivalence point, pH  $\approx$  7
- 3) If possible, determine the  $pK_a$  or  $pK_b$  of the analyte (and identify if your value is  $pK_a$  or  $pK_b$ ).

n/a

Graph 4



- 1) What type of titration? WA w/ SB
- 2) At the equivalence point, pH  $\approx$  9
- 3) If possible, determine the  $pK_a$  or  $pK_b$  of the analyte (and identify if your value is  $pK_a$  or  $pK_b$ ).

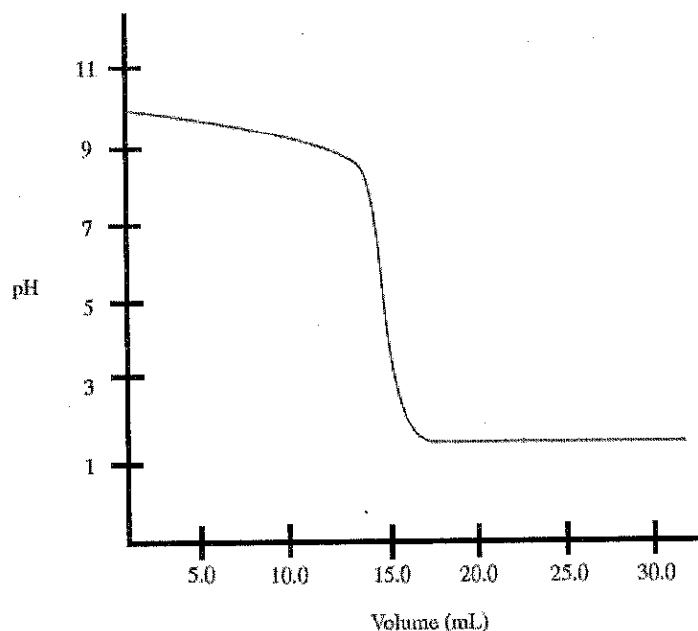
$$pK_a = 4.5$$

$$K_a = 1 \times 10^{-4.5}$$

### Multiple Choice Practice

Use the following information to answer questions 1-5.

The following curve is obtained during the titration of 30.0 mL of 1.0 M  $NH_3$ , a weak base, with a strong acid.



1. Why is the solution acidic at equilibrium?
  - a. The strong acid dissociates fully, leaving excess  $[H^+]$  in solution.
  - b. The conjugate acid of  $NH_3$  is the only ion present at equilibrium.
  - c. The water which is being created during the titration acts as an acid.
  - d. The acid is diprotic, donating two protons for every unit dissociated.

2. What is the concentration of the acid?

- a. 0.50 M                      b. 1.0 M                      c. 1.5 M                      **d. 2.0 M**

$$M_a V_a = M_b V_b$$

$$x(15 \text{ mL}) = (1 \text{ M})(30 \text{ mL}) \Rightarrow x = \frac{30}{15} = 2$$

3. What ions are present in significant amounts during the buffer region?

- a.**  $\text{NH}_3$  and  $\text{NH}_4^+$                       b.  $\text{NH}_3$  and  $\text{H}^+$                       c.  $\text{NH}_4^+$  and  $\text{OH}^-$                       d.  $\text{H}_3\text{O}^+$  and  $\text{NH}_3$

4. Which volume on the titration curve corresponds with the region of **maximum buffer efficacy**?  $\Rightarrow \frac{1}{2}$  eq. pt!

- a. 0 mL                      **b.** 7.5 mL                      c. 15 mL                      d. 22.5 mL

5. The titration is completed using an indicator which changes color at the exact equivalence point of the titration. The protonated form of the indicator is  $\text{HIn}$ , and the deprotonated form is  $\text{In}^-$ . At the equivalence point of the reaction:

- a.**  $[\text{HIn}] = [\text{In}^-]$                       b.  $[\text{HIn}] = 1/[\text{In}^-]$                       c.  $[\text{HIn}] = 2[\text{In}^-]$                       d.  $[\text{HIn}] = [\text{In}^-]^2$

### How to Sketch A Titration Curve

#### 1. Shape of curve

- a. Acid titrated with a base (i.e. base added to acid, [acid] unknown): start low and end high pH  
 b. Base titrated with an acid (i.e. acid added to base, [base] unknown): start high and end low pH

#### 2. Starting pH (initial plateau)

- a. Starting pH < 7 if acid titrated with a base (usually  $\text{pH} < 4$ )  
 b. Starting pH > 7 if base titrated with an acid (usually  $\text{pH} > 10$ )

#### 3. Equivalence point Volume (mL): steepest part (inflection point)

- a. Make sure you are using the volume of the solution being added (your titrant)  
 b. Use  $V_A M_A = V_B M_B$

#### 4. Equivalence point pH

- a. Strong acid + strong base:  $\text{pH} = 7$   
 b. Strong acid + weak base:  $\text{pH} < 7$   
 c. Weak acid + strong base:  $\text{pH} > 7$

#### 5. Ending pH (final plateau)

- a. Ending pH > 7 if acid titrated with a base (usually  $\text{pH} > 10$ )  
 b. Ending pH < 7 if base titrated with an acid (usually  $\text{pH} < 4$ )

## Let's Practice!

titrant

RbOH

6. A 30.0 mL sample of 0.215 M hydroiodic acid completely neutralized 21.2 mL of aqueous rubidium hydroxide solution in a titration experiment.

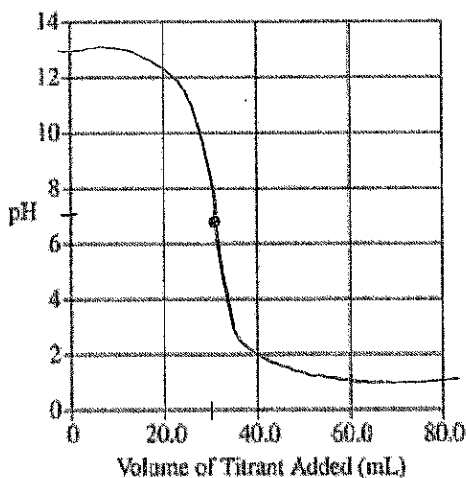
a. Calculate the molarity of the initial rubidium hydroxide solution.

$$M_a V_a = M_b V_b$$

$$(0.215 \text{ M})(30.0 \text{ mL}) = M_b (21.2 \text{ mL})$$

$$M_b = \frac{0.215 \times 30.0}{21.2} = \boxed{0.316 \text{ M}}$$

b. Sketch the curve that would result from this titration experiment on the grid below.



SB w/ SA!

2. It is found that 24.68 mL of 0.1165 M NaOH is needed to titrate 0.2931 g of a solid, unknown monoprotic acid to the end point. Calculate the molar mass of the acid.

a. Calculate the moles of unknown acid in your sample.

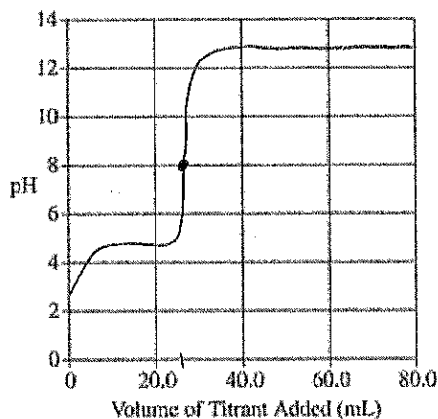
$$\text{moles acid} = \text{mol base (@ eq. pt)}$$

$$= M_b V_b = (0.1165 \text{ M})(0.02468 \text{ L}) = \boxed{0.002875 \text{ mol HA}}$$

b. Determine the molar mass of the unknown acid.

$$\text{MM(HA)} = \frac{0.2931 \text{ g}}{0.002875 \text{ mol}} = \boxed{101.9 \text{ g/mol}}$$

c. Sketch the curve that would result from this titration experiment on the grid below.



WA w/ SB