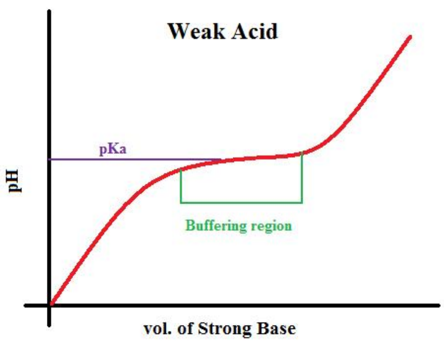
15.4 - 15.5 - Titrations & Indicators



Titration of a weak acid with a strong base

Titrations

Chemists often determine concentrations by reacting a chemical of known concentration with another with an unknown concentration.

Called titration, this method is often employed to determine acid or base concentration.

The net equation for strong acid-base titrations is:

$$H^+ + OH^- = H_2O$$

A tool used for this is a buret, and since titrations are conducted with mL amounts, a convenient unit of concentration is a millimole (mmol):

$$Molarity = \frac{mol\ solution}{L\ solution} = \frac{mmol\ solution}{mL\ solution}$$

5. Titration of Strong Acid - Strong Base

Consider the titration of 50.0 mL of 0.200 M HNO_3, titrated with increasing aliquots (measured amounts) of 0.100 M NaOH.
Calculate the pH after the following additions are made:

A. No NaOH added yet,

B. 10.0 mL added,

C. 20.0 mL,

D. 50.0 mL,

E. 100.0 mL,

F. 150.0 mL,

G. 200.0 mL.

Titration Answer A & B

A. No NaOH added yet.
pH is calculated directly from HNO_3 concentration:

$$pH = -\log[0.200] = \boxed{0.699}$$

B. 10.0 mL added,
The starting amount of HNO_3 (in mmol) is:

$$50.0\,mL \bullet \frac{0.200\,mol}{1000.0\,mL} = 0.0100\,mol = 10.0\,mmol\ HNO_3$$

The amount of NaOH (in mmol) added:

$$10.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.00100\,mol = 1.00\,mmol\ NaOH$$

Titration Answer B (Slide 2)

B. Stoichiometry requires a balanced reaction:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Post-Reaction amounts:
HNO_3: 10.0 mmol - 1.00 mmol = 9.0 mmol

New volume: 50.0 mL + 10.0 mL = 60.0 mL

New $[H^+]$ concentration:

$$[H^+] = \frac{mmol}{mL} = \frac{9.0\,mmol}{60.0\,mL} = 0.15\,M$$

pH:

$$pH = -\log[0.15] = \boxed{0.82}$$

Titration Answer C

C. 20.0 mL added.

NaOH (in mmol) added:

$$20.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.00200\,mol = 2.00\,mmol\ NaOH$$

Post-Reaction amounts:
HNO_3: 10.0 mmol - 2.00 mmol = 8.0 mmol

Volume: 50.0 mL + 20.0 mL = 70.0 mL

New $[H^+]$ concentration:

$$[H^+] = \frac{mmol}{mL} = \frac{8.0\,mmol}{70.0\,mL} = 0.11\,M$$

pH:

$$pH = -\log[0.11] = \boxed{0.96}$$

Titration Answer D

D. 50.0 mL added.

NaOH (in mmol) added:

$$50.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.00500\,mol = 5.00\,mmol\ NaOH$$

Post-Reaction amounts:

HNO_3: 10.0 mmol - 5.00 mmol = 5.0 mmol

Volume: 50.0 mL + 50.0 mL = 100.0 mL

New $[H^+]$ concentration:

$$[H^+] = \frac{mmol}{mL} = \frac{5.0\,mmol}{100.0\,mL} = 0.50\,M$$

pH:

$$pH = -\log[0.05] = \boxed{1.30}$$

Titration Answer E

E. 100.0 mL added.

NaOH (in mmol) added:

$$100.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.0100\,mol = 10.0\,mmol\ NaOH$$

Post-Reaction amounts:

HNO_3: 10.0 mmol - 10.00 mmol = 0.0 mmol

Here, exactly equal amounts of acid and base have reacted, so the solution has reached its stoichiometric point, or equivalence point.

The pH is 7.0, as the H^+ and OH^- ions are equal.

pH:

Titration Answer F

F. 150.0 mL added.

NaOH (in mmol) added:

$$150.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.01500\,mol = 15.00\,mmol\ NaOH$$

Post-Reaction amounts - NaOH is in excess:

NaOH: 15.0 mmol - 10.0 mmol = 5.0 mmol NaOH

Volume: 150.0 mL + 50.0 mL = 200.0 mL

New $[OH^-]$ concentration:

$$[OH^+] = \frac{mmol}{mL} = \frac{5.0\,mmol}{200.0\,mL} = 0.025\,M$$

pOH:

$$pOH = -\log[0.025] = 1.60$$

$$pH = 14.00 - 1.60 = \boxed{12.40}$$

Titration Answer G

G. 200.0 mL added.

NaOH (in mmol) added:

$$200.0\,mL \bullet \frac{0.100\,mol}{1000.0\,mL} = 0.0200\,mol = 20.00\,mmol\ NaOH$$

Post-Reaction amounts - NaOH is in excess:

NaOH: 20.0 mmol - 10.0 mmol = 10.0 mmol NaOH

Volume: 200.0 mL + 50.0 mL = 250.0 mL

New $[OH^-]$ concentration:

$$[OH^+] = \frac{mmol}{mL} = \frac{10.0\,mmol}{250.0\,mL} = 0.040\,M$$

pOH:

$$pOH = -\log[0.040] = 1.40$$

$$pH = 14.00 - 1.40 = \boxed{12.60}$$

Titration Terms

Stoichiometric Point (Equivalence Point): Point in a titration at which $[H^+]$ and $[OH^-]$ are equal.

For a strong acid-base titration, this is at pH = 7, but will not be so for a weak vs. strong acid-base titration.

Halfway Point: In a weak acid vs. strong base, or strong acid vs. weak base titration, it is the point at which half of the weak acid (or base) has reacted, forming its conjugated base (or acid).

At the Halfway Point: $[H^+] = K_a$, and $pH = pK_a$

pH Curves

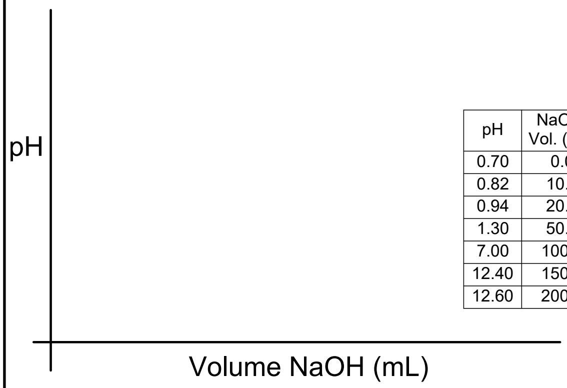
A plot of pH (y-axis) vs. volume of titrant (x-axis) produces a pH curve.

6. Produce a pH curve, using this data from the previous problem.

pH	NaOH Volume (mL)
0.70	0.0
0.82	10.0
0.94	20.0
1.30	50.0
7.00	100.0
12.40	150.0
12.60	200.0

Graphing pH

6. pH curve:



pH	NaOH Vol. (mL)
0.70	0.0
0.82	10.0
0.94	20.0
1.30	50.0
7.00	100.0
12.40	150.0
12.60	200.0

Weak vs. Strong Acids/Bases

When titrating a weak acid with a strong base (or vice versa), a new strategy must be used:

1. **Stoichiometry** first determines the molar (or mmolar) amount of weak acid/base.

2. An **equilibrium calculation** follows, which determines the position of the reaction.

3. A **pH Calculation** is the final step.

7. Weak Acid-Strong Base Titration

50.0 mL of 0.10 M acetic acid (K_a = 1.8 E -5) is titrated with 0.10 M NaOH. What is the pH at the following volumes?

A. 0.0 mL.

B. 10.0 mL

C. 25.0 mL

D. 50.0 mL

E. 75.0 mL

Getting Started on #7.

A. 0.0 mL NaOH: pH stems from the equilibrium expression of 0.10 M acetic acid.

$$pK_a = 1.8E-5 = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \approx \frac{x^2}{0.10}$$

$$x \approx 1.34E-3M$$

Then pH: $pH = -\log(1.34E-3) = \boxed{2.87}$

B. 10.0 mL NaOH added:

First, calculate the initial amount of acid:

$$50.0\,mL \bullet \frac{0.10\,mol}{1000.0\,mL} = 0.0050\,mol = 5.0\,mmol\,CH_3COOH$$

Then base added:

$$10.0\,mL \bullet \frac{0.10\,mol}{1000.0\,mL} = 0.0010\,mol = 1.0\,mmol\,NaOH$$

7.B Continued (Slide 1)

B. Determine the balanced reaction, and calculate equilibrium amounts using stoichiometry:

Reaction: $NaOH + CH_3COOH \rightarrow Na^+ + CH_3COO^- + H_2O$

Equilibrium amounts:
acetic acid: 5.0 mmol - 1.0 mmol = 4.0 mmol
acetate ion: 1.0 mmol

Equilibrium concentrations:

Acid: $[CH_3COOH] = \frac{mmol}{mL} = \frac{4.0\,mmol}{60.0\,mL} = 0.067\,M$

Acetate: $[CH_3COO^-] = \frac{mmol}{mL} = \frac{1.0\,mmol}{60.0\,mL} = 0.017\,M$

7.B Continued (Slide 2)

B. Next, equilibrium calculation:

$$K_a = 1.8E-5 = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[x][0.0167-x]}{[0.0667-x]} \approx \frac{x(0.017)}{0.067}$$

$$[H^+] \approx x \approx 7.1E-5M$$

Finally pH:

$$pH = -\log(7.1E-5) = \boxed{4.15}$$

7.C Answer (Slide 1)

C. 25.0 mL NaOH added:

$$25.0\,mL \bullet \frac{0.10\,mol}{1000.0\,mL} = 0.0025\,mol = 2.5\,mmol\ NaOH$$

Equilibrium amounts:
acetic acid: 5.0 mmol - 2.5 mmol = 2.5 mmol
acetate ion: = 2.5 mmol.

This is halfway point of the titration, where half of the acetic acid has been consumed by the base.

Equilibrium concentrations:

Acid: $[CH_3COOH] = \frac{mmol}{mL} = \frac{2.5\,mmol}{75\,mL} = 0.033\,M$

Acetate: $[CH_3COO^-] = \frac{mmol}{mL} = \frac{2.5\,mmol}{75.0\,mL} = 0.033\,M$

7.B Continued (Slide 2)

B. Next, equilibrium calculation:

$$K_a = 1.8E-5 = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[x][0.033-x]}{[0.033-x]} = x$$

$[H^+] = x = 1.8E-5M$

Finally pH:

$$pH = -\log(1.8E-5) = \boxed{4.74}$$

7.D Answer (Slide 1)

D. 50.0 mL NaOH added:

$$50.0\,mL \bullet \frac{0.10\,mol}{1000.0\,mL} = 0.0050\,mol = 5.0\,mmol\ NaOH$$

Equilibrium amounts:
acetic acid: 5.0 mmol - 5.0 mmol = 0.0 mmol
acetate ion: = 5.0 mmol.

This is equivalence point of the titration, where all acetic acid has been consumed by the base.

In the resulting solution, we must use a new equilibrium expression, accounting for the basic acetate ion, starting with its concentration:

$$M_{CH_3COO^-} = \frac{5.0\,mmol}{100.0\,mL} = 0.050\,M$$

7.D Answer (Slide 2)

The reaction:

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

Since this is a basic solution, we need K_b:

$$K_b = \frac{1.0E-14}{K_a} = \frac{1.0E-14}{1.8E-5} = 5.6E-10$$

The equilibrium calculation, followed by the pOH calculation, then pH:

$$K_b = 5.6E-10 = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = \frac{[x][x]}{[0.050]} \approx \frac{x^2}{0.050}$$

$[OH^+] \approx x \approx 5.3E-6M$

$$pOH = -\log(5.3E-6) = 5.27$$

$$pH = 14 - 5.27 = \boxed{8.73}$$

Note: at weak acid/base equivalence, pH is not 7.00.

7. E Answer

E. 75.0 mL NaOH added.

Since this is past the equivalence point, the addition of more NaOH will add hydroxide ions, contributing directly to the pH calculation.

Calculate excess NaOH:

$$75.0\,mL \bullet \frac{0.10\,mol}{1000.0\,mL} = 0.075\,mol = 7.5\,mmol\ NaOH$$

7.5 mmol NaOH (added) - 5.0 mmol NaOH (used) = 2.5 mmol NaOH (unreacted).

NaOH concentration: $M_{NaOH} = \frac{2.5\,mmol}{125.0\,mL} = 0.020\,M$

pH: $pOH = -\log(0.020) = 1.70$

$$pH = 14 - 5.27 = \boxed{12.30}$$

Titration Curve Features

Depending on what is being titrated, and how concentrated the sample and titrant are, titration curves will have different shapes, but will have some features which are the same for all.

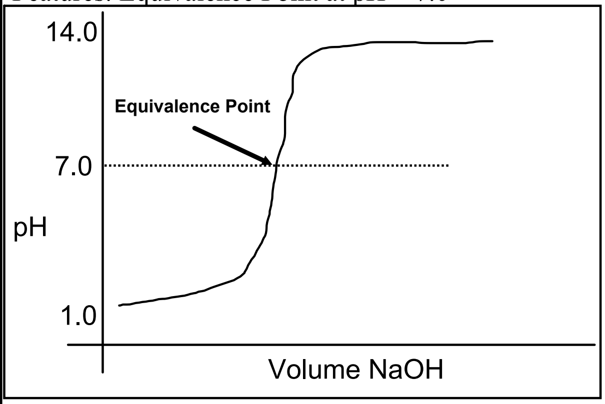
In all cases, we consider the titrant to be a strong acid/base.

Dependence on concentration: Acids/bases titration curves are steeper when a more concentrated titrant is used: less volume of titrant is required to produce a large pH change.

Titration Curves (Slide 1)

Strong acid sample.

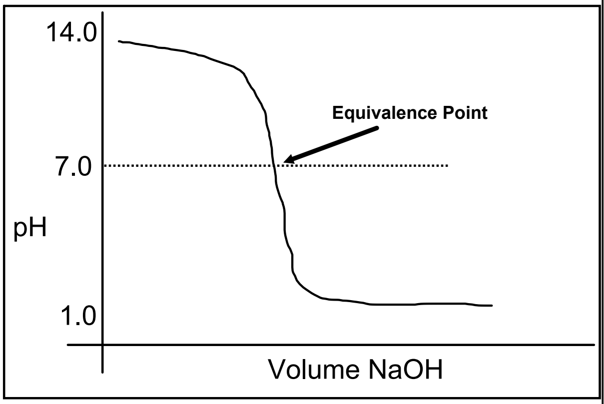
Features: Equivalence Point at pH = 7.0



Titration Curves (Slide 2)

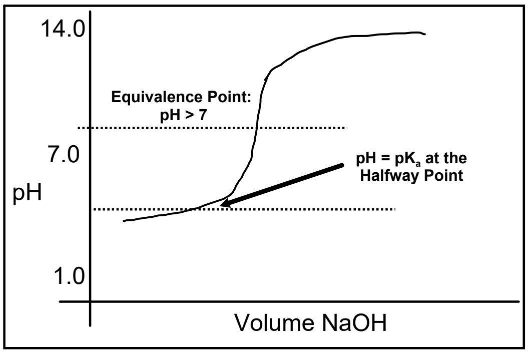
Strong base sample.

Features: Equivalence Point at pH = 7.0



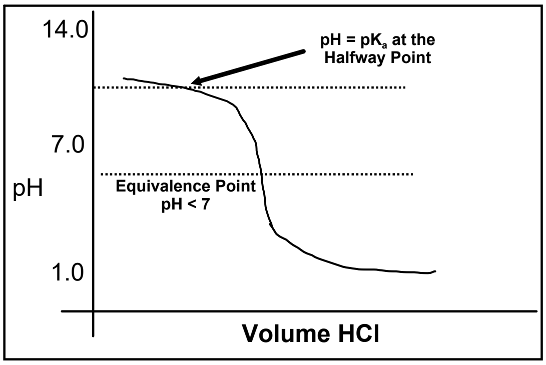
Titration Curves (Slide 3)

Weak acid as sample:
Features: A. pH = pK_a at the Halfway Point.
B. Equivalence Point pH > 7.0 - conjugate base raises pH as it accepts protons.



Titration Curves (Slide 4)

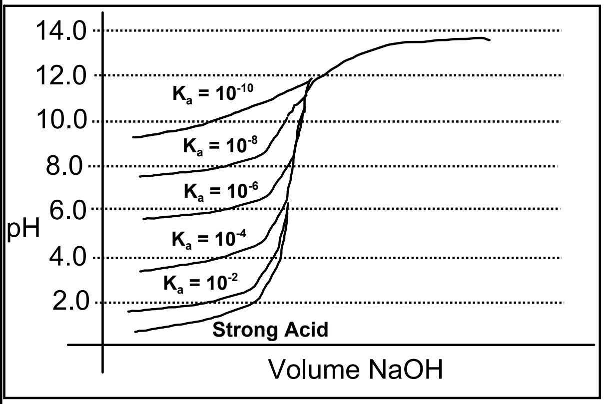
Weak base sample.
Features: A. pH = pK_a at the Halfway Point.
B. Equivalence Point pH < 7.0 - conjugate acid lowers pH as it releases protons.



Titration Curves (Slide 5)

Comparing multiple weak acid samples:

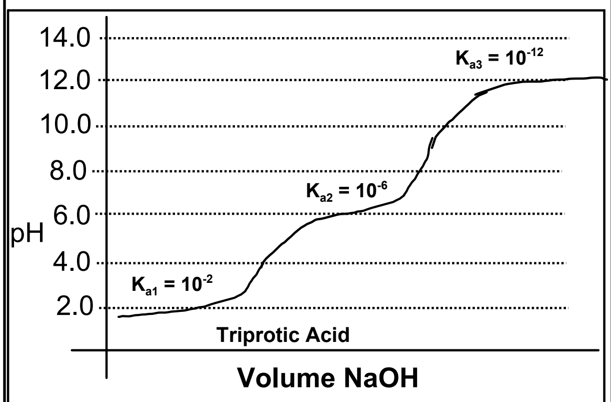
Features: pH = pK_a at the Halfway Point.



Titration Curves (Slide 6)

Polyprotic acid sample:

Features: pH = pK_a at multiple points.



Measuring pH

Two common methods of determining pH in the laboratory are:
A. Use a meter.
B. Use a color changing, pH sensitive Indicator. Indicators are molecules that will react with acids and bases, and change colors as a threshold pH is crossed.

Ex. Phenolpthalein changes from clear to pink at a pH of around 9.0 as pH is increasing. Demo.

Ex: Bromothymol Blue changes from yellow through green to blue around a pH of 7.0 as pH increasing. Demo.

Homework

Preview 12.3

12.1-.2 Problems in your Booklet
Due: Next Class