Titration Curves

1. Volumetric technique used to determine quantities. Acid-base titrations are one application of titration.
2. In lab we will look at three types of acid-base titration curves. In lecture we will give an overview and highlight the main points for the different types of titrations.
3. We will also look at polyprotic acid titration curves.

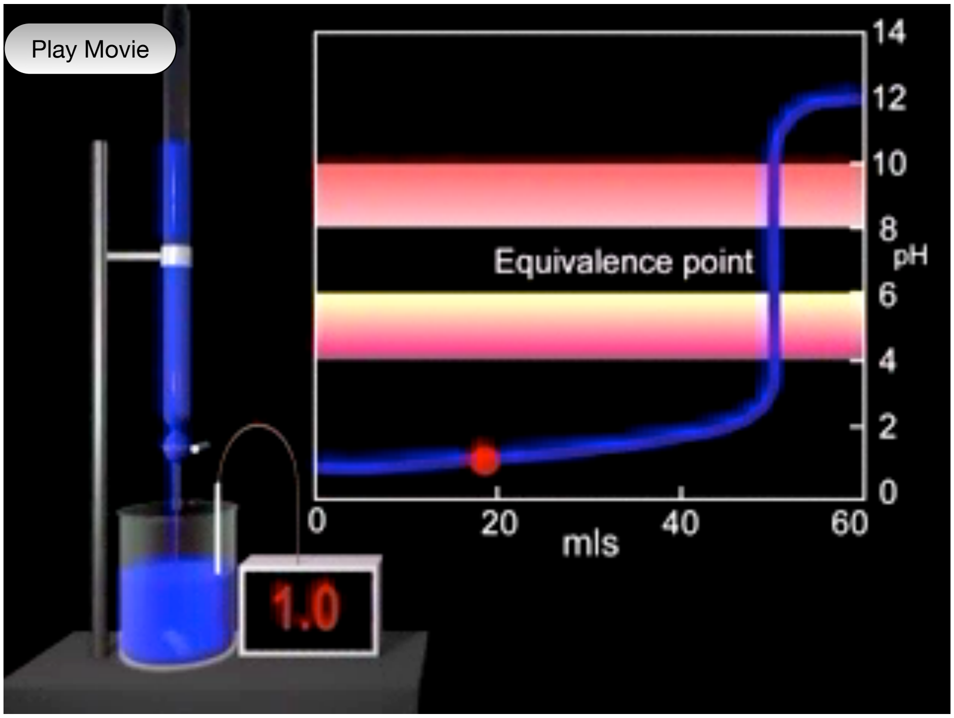
The types of curves we will discuss:

1. Strong Acid titrated with a Strong Base
2. Strong Base titrated with a Strong Acid
3. Weak Acid titrated with a Strong Base
4. Polyprotic Acid Titrated with a Strong Base
5. Weak Base titrated with a Strong Acid

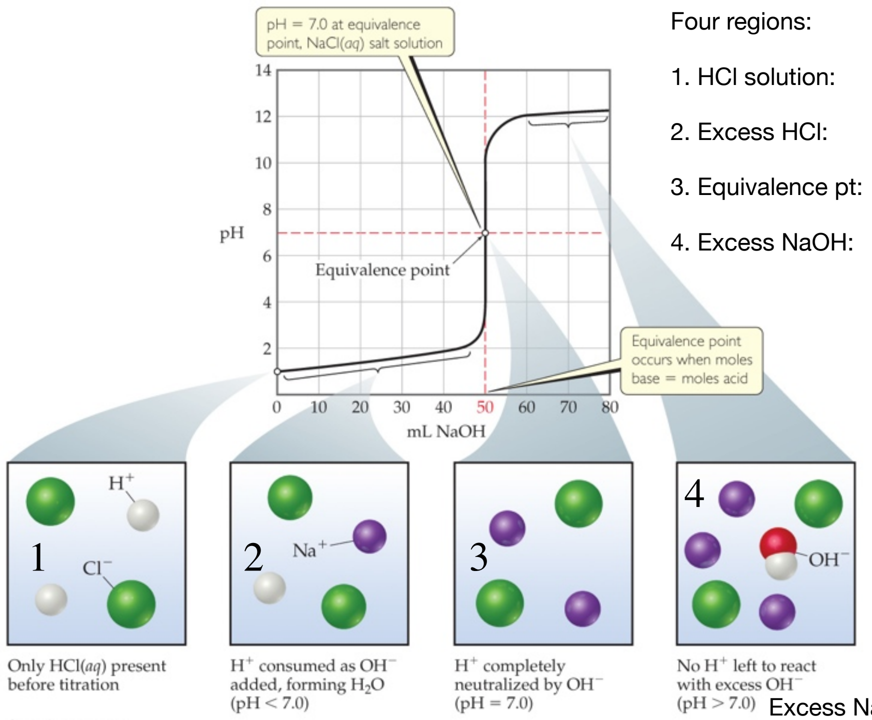
Definitions:

1. Equivalence point: moles Acid = moles Base.
2. End point: when the indicator changes color ≠ equivalence pt.

HCl Titrated with NaOH



HCl Titrated with NaOH



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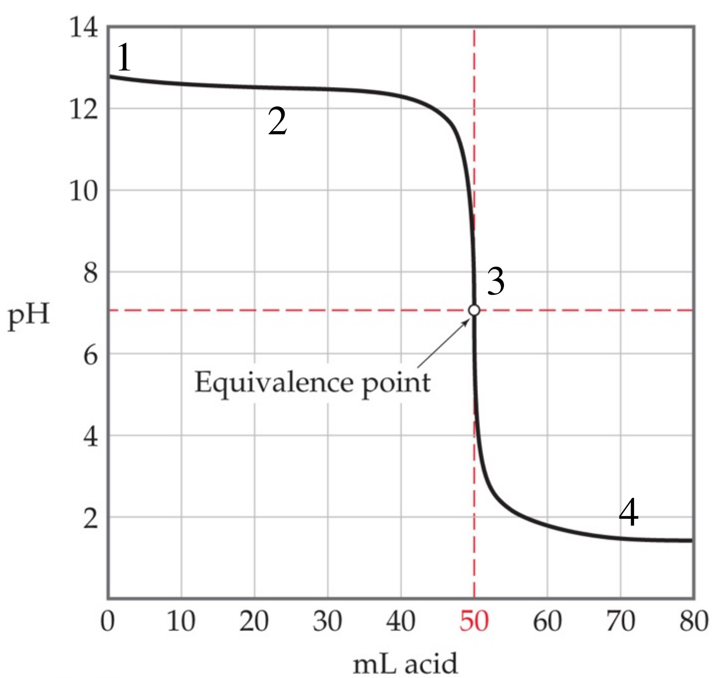
Excess HCl

Excess NaOH

Four regions:

1. HCl solution: pH = $-\log[HCl]_{initial}$
2. Excess HCl: pH = $-\log[HCl]_{excess}$
3. Equivalence pt: pH = 7.00
4. Excess NaOH: pOH = $-\log[NaOH]_{excess}$

Strong Base Titrated with a Strong Acid



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Identify the Four Regions:

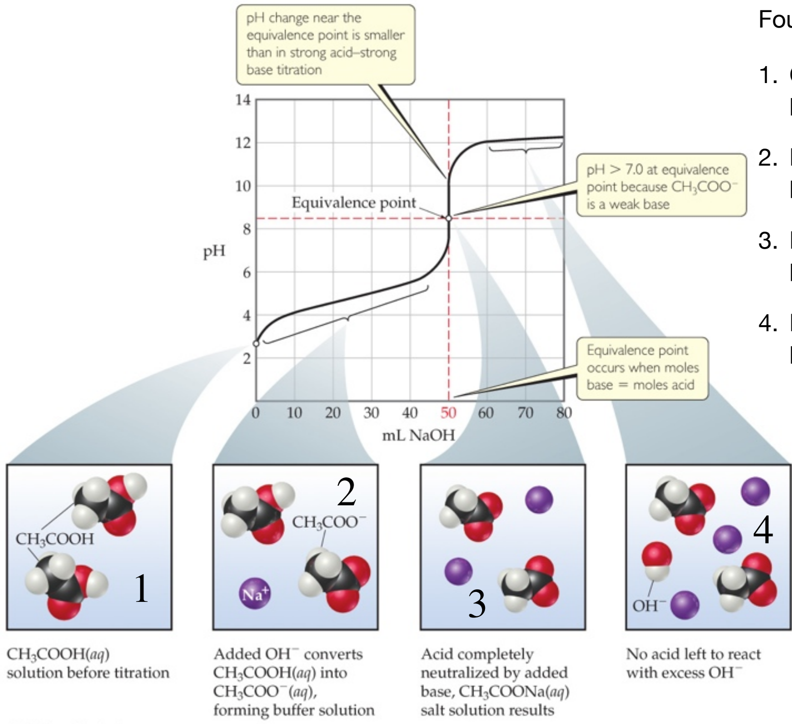
1.

2.

3.

4.

Acetic Acid Titrated with a Strong Base



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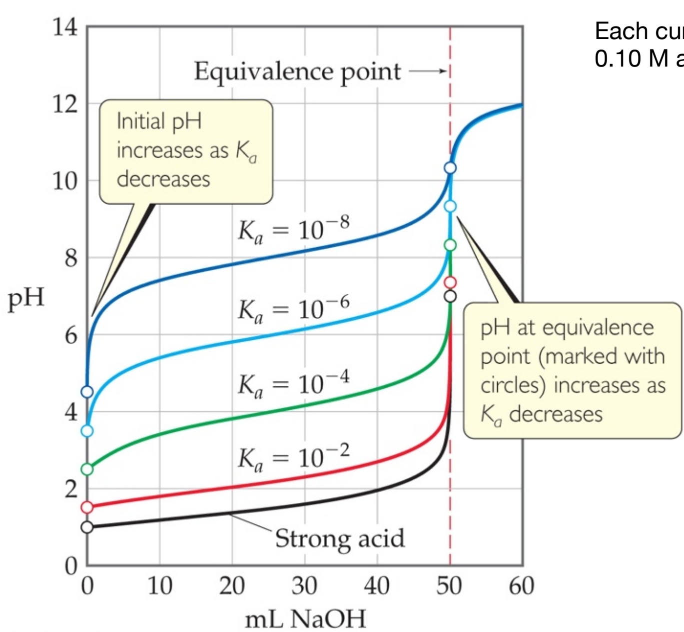
Four regions:

1. CH_3COOH solution:
   pH from K_a and $[CH_3COOH]_{initial}$
2. Buffer Region:
   pH from H-H equation
3. Equivalence pt: pH > 7.00
   pH from K_b and $[NaCH_3COO]_{eq.\ pt.}$
4. Excess NaOH:
   pOH ≈ -log$[NaOH]_{excess}$

The Effect of K_a on a Weak Acid Titration Curve



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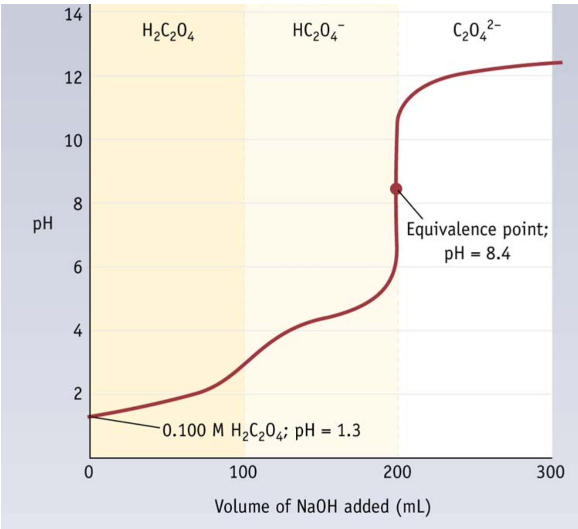
Each curve represents titration of 50-mL of a 0.10 M acid with 0.10 M NaOH.

Questions: For acid solutions with the same concentration titrated with the same strong base solution:

1. What is the trend for the initial pH of the acid solutions?
2. What is the trend for the magnitude of the rapid pH increase near the equivalence point.
3. What is the trend for the pH at the equivalence point of the titrated solutions?
4. What do you notice about the equivalence point volume?

Oxalic Acid Titrated with a Strong Base
($K_{a1} = 5.9\text{x}10^{-2}$; $K_{a2} = 6.4\text{x}10^{-5}$)

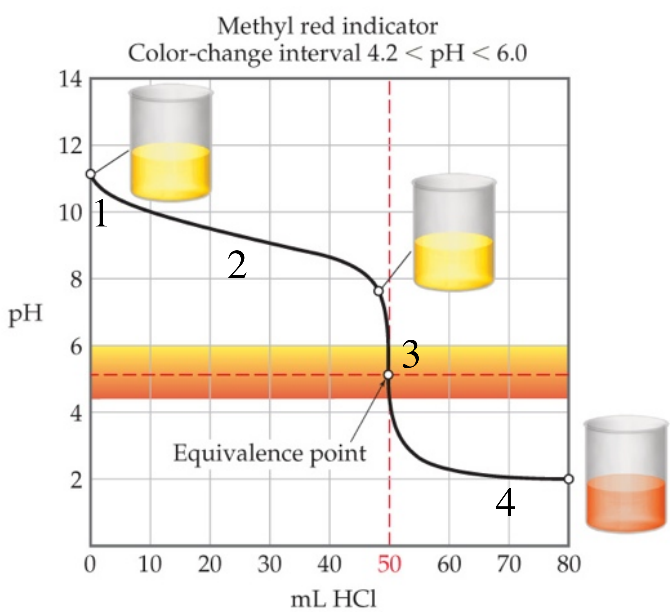


1. The pH before titration is determined by the weak acid concentration and K_{a1}. Must use quadratic!
2. After the titration begins until the first equivalence point has been reached, the pH is determined by the common ion effect and K_{a1}. Must use quadratic! H-H equation DOES NOT apply in the case of oxalic acid.
3. Locate the first equivalence point. What is left in solution at this point? Is the solution acidic or basic at this point? Explain why.
4. From the first equivalence point until the second equivalence point, the pH is determined by K_{a2}. Why? Is there a common ion effect?
5. At the second equivalence point the pH is basic. Why?
6. Beyond the second equivalence point the pH is determined by excess base added.

Weak Base Titrated with a Strong Acid

Four regions:

1. NH_3 solution:
   pH from K_b and $[NH_3]_{initial}$
2. Buffer Region:
   pH from H-H equation
3. Equivalence pt: pH < 7.00
   pH from K_a and $[NH_4Cl]_{eq.\ pt.}$
4. Excess HCl:
   pH ≈ $-\log[HCl]_{excess}$



Suitable indicator because equivalence point falls within the color-change interval

Acid-Base Indicators

Acid-base indicators are themselves weak acids or bases. Their color depends upon whether the acid (PROTONATED) or base (DEPROTONATED) form dominates in solution. This is pH dependent.
Using HInd to abbreviate a PROTONATED indicator:

$$HInd(aq) + H_2O(l) \rightleftharpoons Ind^{-}(aq) + H_3O^{+}(aq)$$

(acid form) (base form)

The acid and base forms ***have different colors*** in solution. We see a color change when one form is converted into another. As with all weak acids, the H-H equation applies where pK_a refers to the *HInd*.

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

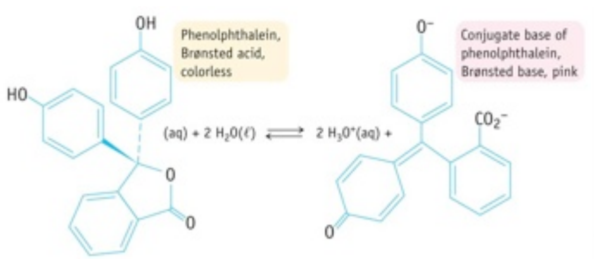
$$\frac{[Ind^-]}{[HInd]} = \frac{K_a}{[H_3O^+]}$$

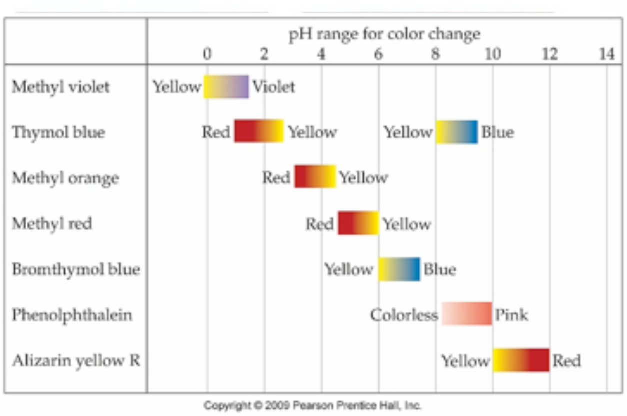
When $pH < pK_a$
the color is determined by the acid form.

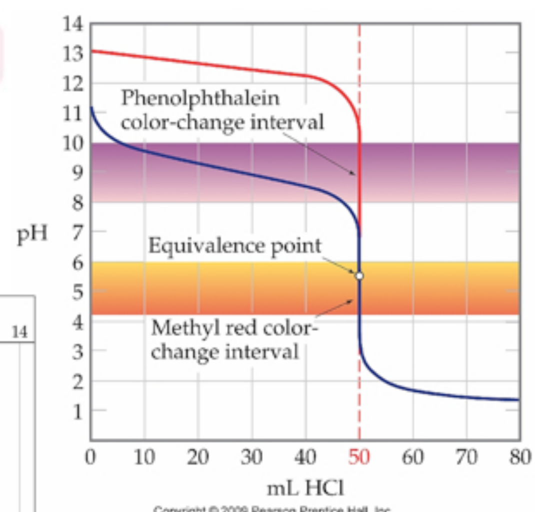
When $pH \approx pK_a$
both forms exist and we see a blend of both colors.

When $pH > pK_a$
the color is determined by the base form.

Example - Phenolphthalein/Methyl Red Indicators







Which indicator(s) shown above would you choose for:
the strong base titration?
the weak base titration?

Are there other indicators that will work as well?

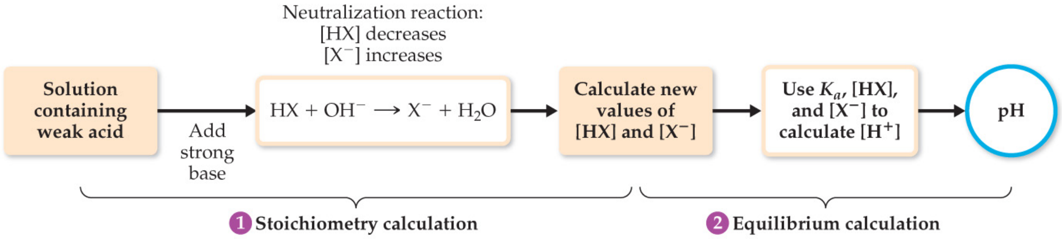
Titration Calculations - Calculating the pH

To calculate the pH along a titration curve you need the following information:

1. Initial M and volume of species titrated.
2. M and volume of the titrant added.
3. K_a (or K_b) of the weak acid (or base) in the system.

Steps to follow:

1. Write the acid-base reaction.
2. Set up a reaction table in moles.
3. Take the reaction 100% forward using limiting reactant principles.
   1. If the strong species is the limiting reagent:
      Find the M of remaining weak species and conjugate. Solve for pH as a common ion problem using K_a. (Can use H-H equation in “buffer region” if “x” is negligible.)
   2. At the equivalence point the pH is determined by conjugate species. Determine the M of the conjugate species and use $K_{conjugate}$ to solve for pH.
   3. Past the equivalence point the concentration of excess titrant determines the pH.



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Sample Titration Calculations

Consider the titration of 20.0 mL of 0.244 M HClO with 0.150 M NaOH. $K_a = 3.0\text{x}10^{-8}$
Write the balanced net-ionic titration reaction:

1. Calculate the starting pH of the 0.244 M HClO solution.
2. Calculate the pH when 10.0 mL of the 0.150 M NaOH is added.
3. Calculate the pH when half the equivalence point volume of NaOH is added.
4. Calculate the pH at the equivalence point.
5. Calculate the pH when an additional 3.0 mL of the 0.150 M NaOH is added past the equivalence point.