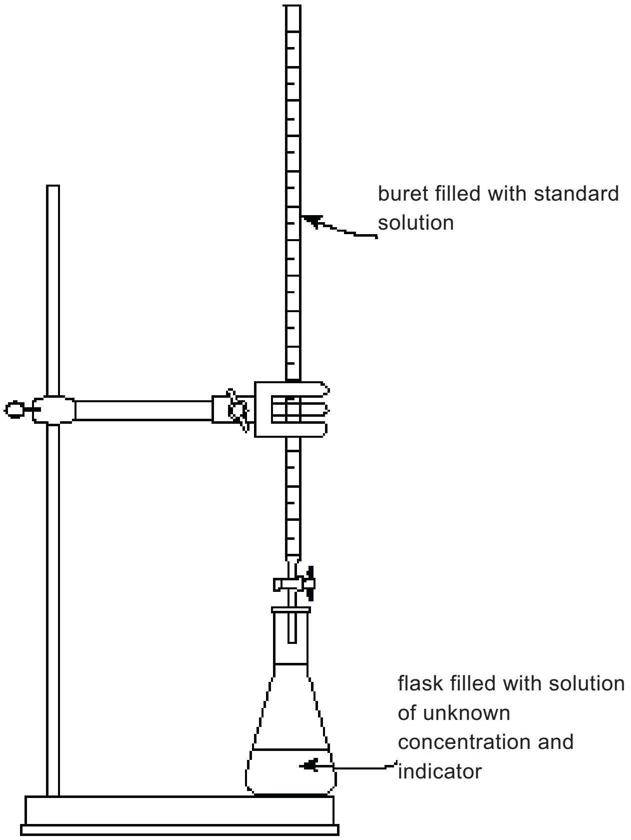
Teacher's Tools® Chemistry

Acid Base Chemistry: Acid-Base Titration: Student Review Notes

Overview

Titration is an analytical procedure that allows for the measurement of the amount of one solution that is required to exactly react with the contents of another solution.
Acid-base titrations are a practical application of acid-base reactions.



A buret is used to measure the precise volume of a standard solution.

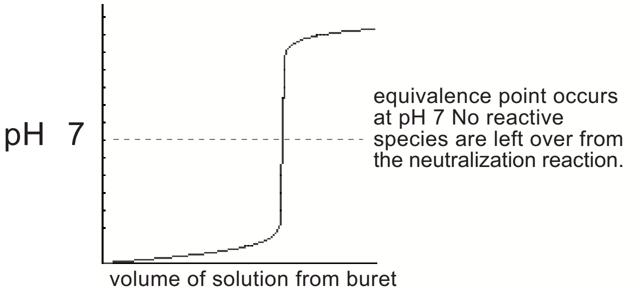
The concentration of the standard solution is known with great precision.

Based upon the reaction stoichiometry, the moles of reactant added to the solution, MV from the buret, yields the number of moles in the sample

In acid-base titrations, an inidicator is used to signal the end of the titration--this is called the endpoint or equivalence point of the titration.

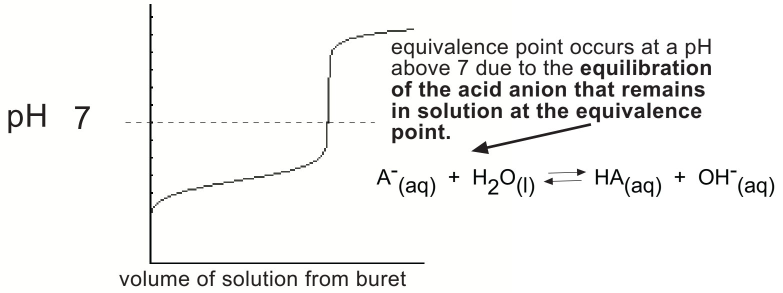
At the endpoint of the titration, the indicator color changes and the pH of the solution in the flask sweeps over a large range of pH values as indicated by the titration curves shown below.

Strong base added to a strong acid



equivalence point occurs at pH 7 No reactive species are left over from the neutralization reaction.

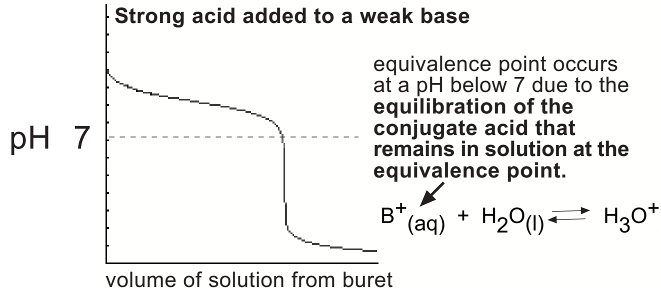
Strong base added to a weak acid



equivalence point occurs at a pH above 7 due to the **equilibration of the acid anion that remains in solution at the equivalence point.**

$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$

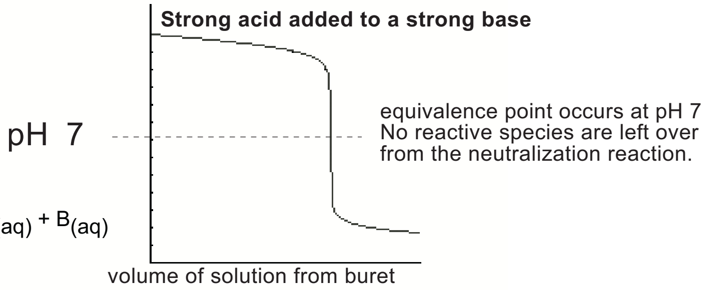
Strong acid added to a weak base



equivalence point occurs at a pH below 7 due to the **equilibration of the conjugate acid that remains in solution at the equivalence point.**

$B^+_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + B_{(aq)}$

Strong acid added to a strong base



equivalence point occurs at pH 7 No reactive species are left over from the neutralization reaction.

Standardizing a Solution

The question is, how do you determine the concentration of the solution in the buret to a high degree of accuracy? The problem is that you can measure mass very accurately but it's not quite as easy to measure a large volume, like a liter, that accurately. To complicate matters even more, NaOH, the strong base used in most titrations, **deliquesces.** That means that it absorbs water. Therefore, when you measure out a mass of NaOH its very likely that you are also measuring an unkown mass of water.
The standardization of NaOH solutions is therefore a common first step in acid-base titration experiments.

1. Use the accuracy of an analytical balance to measure out a mass of a solid acid. Typically the solid acid is KHP, potassium hydrogen phthalate. $KHC_8H_4O_4$, is a solid monoprotic acid. Once you have accurately recorded the mass of KHP, you calculate the moles by dividing by the molar mass and then you dissolve it in some water. It doesn't matter how much water you use, i.e. you've removed the inaccuracy of measuring a volume of liquid, because you know the moles of H+ to be neutralized is the same as the moles of KHP in solution.

2. Add an indicator like phenophthalene to the KHP solution so that you can accurately determine the endpoint of the titration.

3. Measure out a mass of the solid NaOH and add it to an amount of water that gives you approximately the concentration of NaOH that you want to use.

4. Perform a standardization titration to get an accurate measure of the concentration of the NaOH solution. The KHP and indicator solution goes in the erlenmeyer flask. Fill the buret with the NaOH solution. Carefully add the NaOH solution until the indicator changes color. At that point, you've neutralized all of the acid in solution. The concentration of the NaOH solution is therefore = (moles KHP)/(volume change of the buret).

Now you are ready to perform a titration experment with a standardized solution.

Here is an example of the calculation:

A sample of 0.6105 g of KHP is dissolved in water and titrated with 29.75 mL of NaOH solution. Calculate the concentration of the NaOH solution.

$$\text{mole KHP} = \frac{(0.6105\ \text{g})}{(204.23\ \text{g/mol})} = 0.002989\ \text{mole of KHP}$$

moles KHP = moles of H^+ neutralized = moles of OH^- added to the solution = 0.002989 moles

$$\text{Concentration of NaOH solution} = (0.002989\ \text{mol})/(.02975\ \text{L}) = \underset{\uparrow}{0.1005\ \text{M}}$$

That is a very accurately known concentration

Indicators

Indicators are molecules (typically weak acids) that change color depending upon whether a proton (H^+) is attached to them or not (whether they are protonated or deprotonated).

$$\boxed{\underset{\substack{\uparrow \\ \text{color 1}}}{HIn_{(aq)}} \rightleftharpoons \underset{\substack{\uparrow \\ \text{color 2}}}{In^-_{(aq)}} + H^+_{(aq)}}$$

For this indicator (weak acid) equilibrium still has to hold: $K_a = \dfrac{[H^+]\,[In^-]}{[HIn]}$

As the solution pH or H^+ concentration changes, the ratio of $\dfrac{[In^-]}{[HIn]}$ must also change to satisfy Ka

Using the Henderson-Hasselbach equation to look at the equilibrium condition, you can see why the solution changes color:

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

The sample pH is changing as solution is added from the burette

The pKa is fixed at the temperature of the titration

The ratio of the number of molecules of each color changes with solution pH in order for the equality of this relationship to be maintained.

You want to choose an indicator such that its pK_a lines up with the pH sweep associated with the endpoint of the titration. This will insure that the ratio of concentrations of the protonated and deprotonated species will change a a number of orders of magnitude near the endpoint of the titration. Here are some typical indicators.

Indicator	K_a	pK_a	pH range	type of titration
methyl orange	6.3×10^{-5}	4.2	4.4 to 3.1 Yellow Red	strong acid into a weak base
methyl red	1.0×10^{-5}	5.0	6.0 to 4.8 Yellow Red	strong acid into a weak base
bromomethyl blue	7.9×10^{-8}	7.1	7.6 to 6.0 Blue Yellow	strong acid-strong base
phenol red	4.0×10^{-8}	7.4	8.0 to 6.6 Red Yellow	stong acid-strong base
phenolphthalene	2.0×10^{-10}	9.7	10.0 to 8.2 Red Colorless	strong base into a weak acid
alizarin yellow-R	1.0×10^{-11}	11.0	12.1 to 10.1 Red Yellow	strong base into a weak acid

Walk Through a Titration Experiment

This is not a titration experiment per se because the concentrations of both solutions are known. It does however take you through the steps of creating a titration curve and you need to understand this.

A sample of 50 mL of 0.75 M acetic acid, CH_3COOH K_a = 1.8 and 10^{-5}, is titrated with 0.950 M NaOH.
What is the pH:

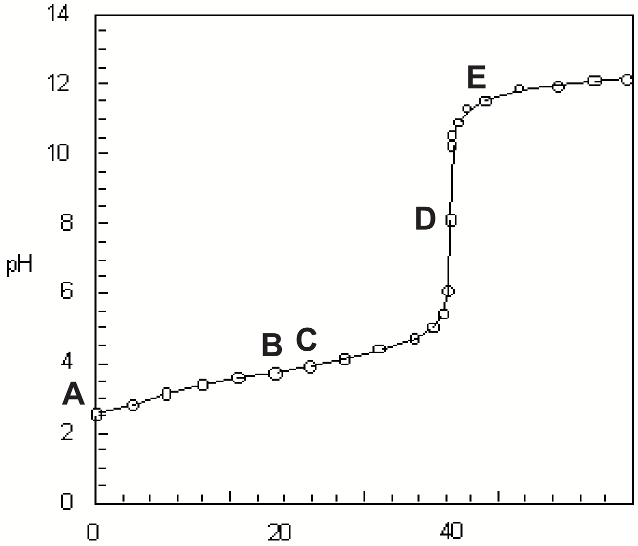
A) before the titration begins

B) at the half-equivalence point

C) after 25 mL of NaOH has been added

D) at neutralization

E) after 45.0 mL of NaOH has been added



A) before the titration begins: this is a standard ICE table calculation given the concentration of acetic acid and its acid dissociation constant.

$$HAc_{(aq)} \rightleftarrows H^+_{(aq)} + Ac^-_{(aq)}$$

	$HAc_{(aq)}$	$H^+_{(aq)}$	$Ac^-_{(aq)}$
Initial	0.75	0	0
Change	-x	x	x
Equililbrium	0.75 - x	x	x

$$Ka = \frac{[H^+]\,[Ac^-]}{[HAc]} = \frac{(x)(x)}{(0.75 - x)} = 1.8 \times 10^{-5}$$

$x = [H^+] = 3.7 \times 10^{-3}$ M

pH = 2.4

B) at the half-equivalence point. You should recognize that when you add half as much strong base to a weak acid, you've made a buffer and therefore its easiest to use the Henderson-Hasselbach equation to get the pH.

$$pH = pK_a + \log\frac{[Ac^-]}{[HAc]}$$ at the half-equivalence point, $[Ac^-] = [HAc]$ therefore, $pH = pK_a$

$$pH = pK_a = -\log(1.8 \times 10^{-5}) = 4.7$$

C) after 25 mL of NaOH has been added you can still use the Henderson-Hasselbach equation to get the pH. Just keep track of the moles of HAc that remain and the moles of Ac- that have been created (same as the moles NaOH added).

moles of NaOH added = (.025 L)(0.950 M) = 0.238 moles = moles of Ac^-
moles of HAc initially = (0.50 L)(0.75 M) = 0.375 moles
moles of HAc remaining = 0.375 moles - 0.238 moles = 0.138 moles
Remember that the H-H equation is volume independent.

$$pH = pK_a + \log\frac{[Ac^-]}{[HAc]} = 4.7 + \log\frac{(0.238)}{(0.138)} = 5.0$$

Walk Through a Titration Experiment continued

D) at neutralization: At neutralization, all of the acetic acid in the sample has been reacted with the strong base. What you really need to understand is that this leaves behind a concentraion of reactive species in solution and the pH of the endpoint is determined by the equilibrium of this reactive species. The reactive species is the acid anion and the amount left in solution is the same as the number of moles of acetic acid with which you started. One note of caution, make sure you add the volume of the NaOH to that of the sample when determining the concentration of acetate ion.

Determine the volume of NaOH necessary to reach the endpoint:
moles HAc = 0.0375 moles = (0.950 M)(V) V = .0395 L
The starting concentration of Ac^- = (0.0375 mole)/(.050 L + .0395 L) = 0.419 M
Setup the ICE table and calculate the equilibrium concentrations

$$Ac^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HAc_{(aq)} + OH^-_{(aq)}$$

	$Ac^-_{(aq)}$	$HAc_{(aq)}$	$OH^-_{(aq)}$
Initial	0.419	0	0
Change	-x	x	x
Equililbrium	0.419 - x	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[HAc]\,[OH^-]}{[Ac^-]} = \frac{(x)(x)}{(0.419 - x)}$$

$x = [OH^-] = 1.5 \times 10^{-6}$ M

pH = 8.2

Just as you should expect, the pH at the endpoint of a strong base into weak acid titration is basic.

E) after 45.0 mL of NaOH has been added: After reaching the endpoint, all you are doing by adding more NaOH solution is making a basic solution. There is no more acid to neutralize and the amount of excess OH^- in solution will determine the solution pH. That’s why after the sweep through pH values at the endpoint, the curve returns to a gradual increase with added volume.

Moles of HAc initially = .0375 moles
Moles of NaOH added = (0.950 M)(0.045 L) = 0.0428 moles
Excess moles of NaOH = .005 moles
Total volume of solution = 0.050 L + 0.045 L = 0.095 L
The concentration of excess OH^- = (0.005 moles)/(0.0950 L) = 5.3×10^{-2} M
pOH = 1.3
pH = 12.7