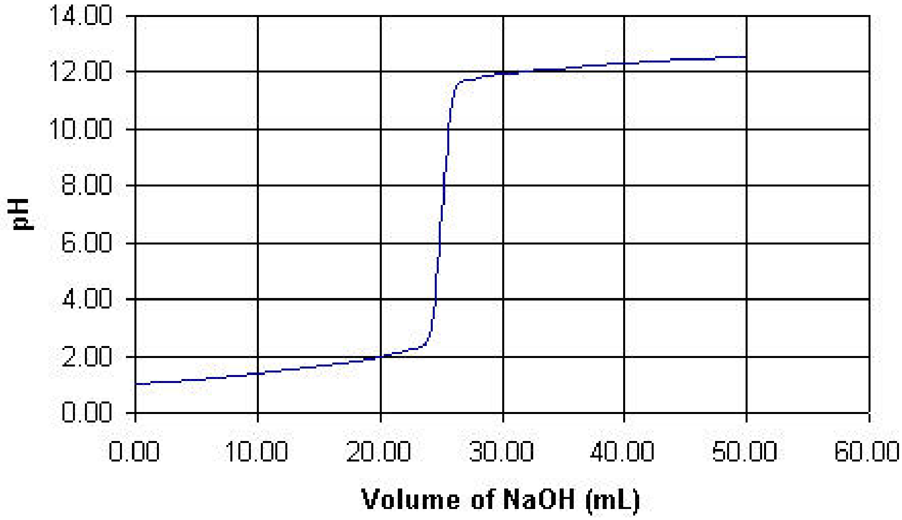
Titration Curves

Titration curves are graphs that represent the pH of a system as the reaction proceeds. It plots volume of titrant (in the buret) added versus the pH.

For example:

Volume of Titrant	0.00	10.11	20.00	22.00	24.00	25.00	26.00	28.00	30.00	40.00	50.00
pH	1.00	1.37	1.95	2.19	2.70	7.00	11.30	11.75	11.96	12.36	12.52



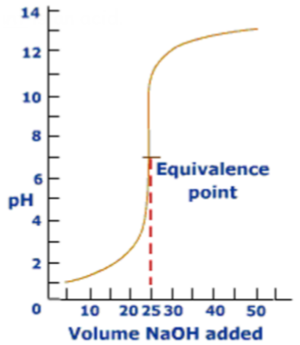
What Titration Curves Tell You

- The initial pH tells you whether the sample is an acid or a base.
- A rise in the curve indicates that the titrant is a base while a decline shows that the titrant is an acid.
- The midpoint of a steep change in pH marks the equivalence point.
- By interpolation you can obtain the information needed to calculate the concentration of the unknown in an acid-base reaction.

Strong Acid-Strong Base Titrations

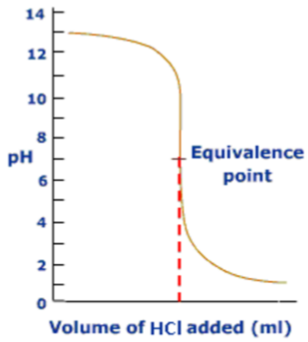
sample is a strong acid

titrant is a strong base



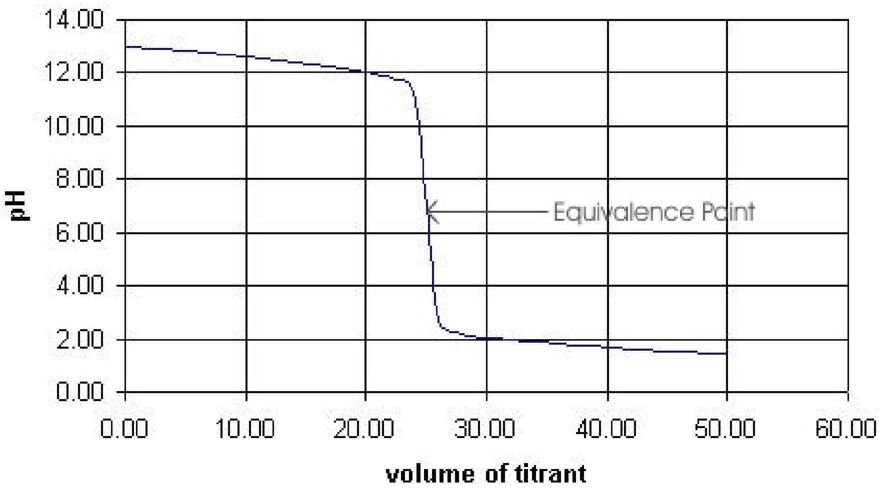
sample is a strong base

titrant is a strong acid



Sample problem 1

The following graph represents a titration between NaOH(aq) and standardized solution of 0.100mol/L HCl(aq)



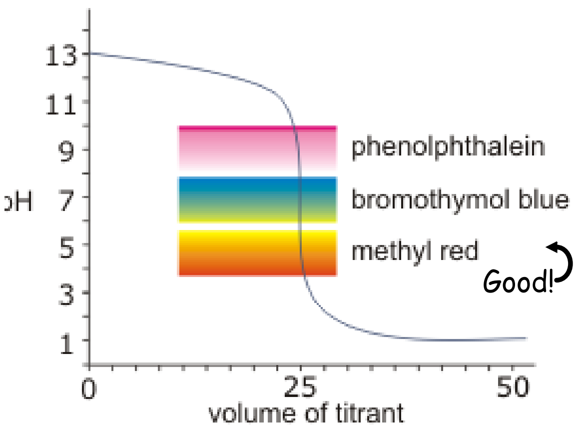
The equivalence point here is when the pH is 7. At this point the volume of NaOH is 25.00mL. You can calculate the concentration of the solution at this point:

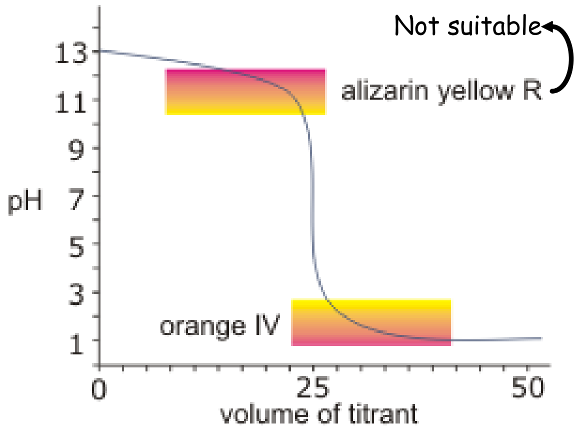
$$C_{NaOH} = 25.00\text{ mL HCl} \times 0.100\,M \times \frac{1\text{ mol NaOH}}{1\text{ mol HCl}} \times \frac{1}{25.00\text{ mL}}$$

$$= 0.100\,M\text{ NaOH}$$

Choosing the Right Indicator

For a strong acid-strong base titration, the indicator should have a range between 4 and 10. Otherwise the colour change will not happen during the steep part of the curve. You will be unable to determine the equivalence point:



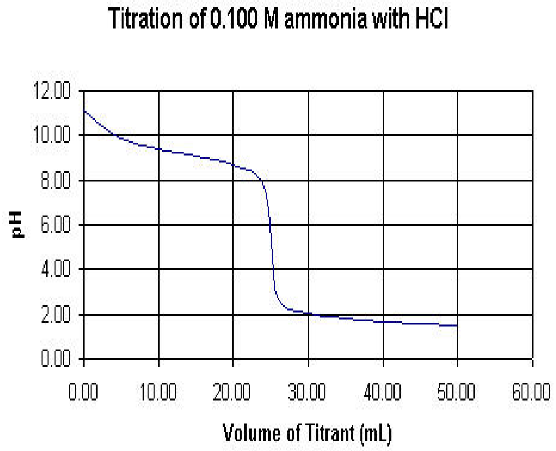


When a strong acid is titrated with a strong base, the pattern is reversed.

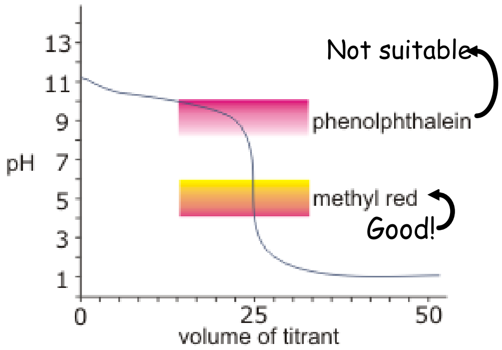
Strong Acid-Weak Base Titrations

Consider the full chemical equation and the Brønsted-Lowry equation for the reaction between ammonia and hydrochloric acid: Full: $NH_{3(aq)}$ + $HCl_{(aq)}$ → $NH_4Cl_{(aq)}$

Bronsted-Lowry: $NH_{3(aq)}$ + $H_3O^+_{(aq)}$ → $NH_4^+{}_{(aq)}$ + $H_2O_{(l)}$



The range is much narrower for indicators here, between 7 and 3:

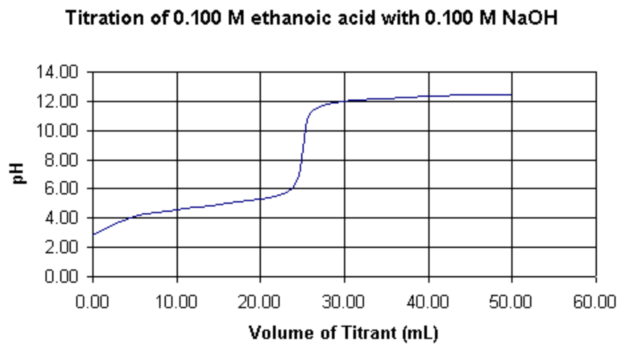


The initial pH (about 11) is lower than it would be if the sample was completely ionized in water (it would be about 13), so the sample is a weak base.

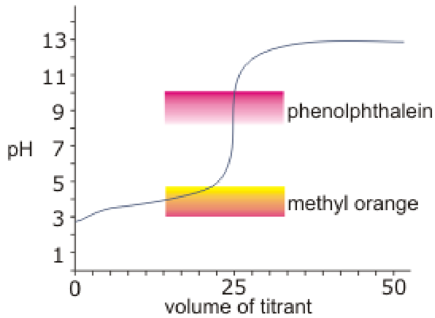
Strong Base-Weak Acid Titrations

The titration of a weak acid with strong base produces a curve similar to the one for a weak base-strong acid titration. The obvious difference is that pH increases with the addition of titrant.

Consider the reaction between sodium hydroxide and ethanoic acid:



Here, phenolphthalein is a good indicator, methyl orange is not:

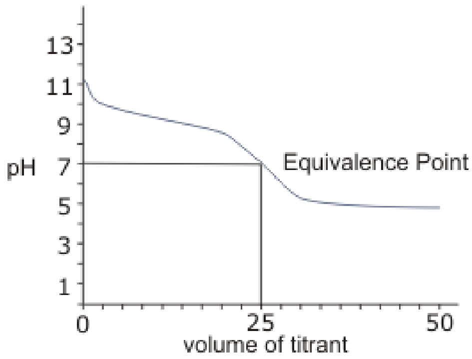


The initial pH (about 3) suggests that the acid is weak.

Weak Acid-Weak Base Titrations

Consider the reaction between ammonia and ethanoic acid:

$$NH_{3\,(aq)} \quad + \quad CH_3COOH_{(aq)} \quad \rightleftharpoons \quad NH_{4\,(aq)}^{+} \quad + \quad CH_3COO^{-}_{(aq)}$$



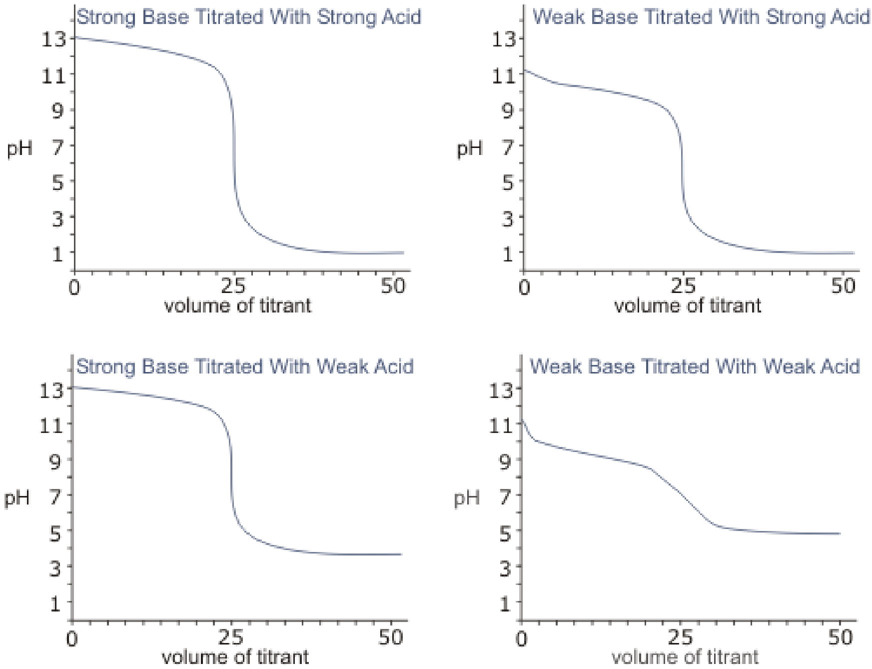
Notice that the reaction is not stoichiometric - it doesn't go to completion, yet there is an equivalence point as you can see from this titration curve.

Since there isn't an abrupt change in pH, the equivalence point cannot be detected using an indicator. The pH change occurs over too broad a volume of titrant to give a proper endpoint.

Summary of Titration Curves

By looking examining the nature of the equivalence point, in combination with the shape of the titration curve, we can interpret the strength and weaknesses of the reagents.
There are eight possibilities :

1. Strong base titrated with strong acid : < starts with high pH, finishes with low pH < equivalence point = 7	**5.** Weak acid titrated with strong base < starts with a medium low pH < equivalence point > 7
2. Strong acid titrated with strong base < starts with low pH, finishes with high pH < equivalence point = 7	**6.** Weak base titrated with strong acid < starts with a medium high pH < equivalence point < 7
3. Strong acid titrated with weak base < starts with a low pH < equivalence point < 7	**7.** Weak base titrated with a weak acid < starts with a medium high pH < equivalence point can't really be predicted
4. Strong base titrated with a weak acid < starts with high pH < equivalence point > 7	**8.** Weak acid titrated with a weak base < starts with a medium low pH < equivalence point can't really be predicted



There are fewer useful indicators for titrations involving weak species than there are for strong acid-strong base titrations.
The equivalence point for strong acid-strong base titrations occurs at pH 7.
The equivalence point for a weak base-strong acid titration is less than pH 7.
The equivalence point for a strong base-weak acid titration is greater than pH 7.

Polybasic Species

Polybasic species <u>can accept more than one proton</u> from an acid.

Terminology: NaF is monobasic (can accept 1 proton)
$CaCO_3$ is dibasic (can accept 2 protons)
$AlPO_4$ is tribasic (can accept 3 protons)

The carbonate ion is polybasic, more specifically it is **dibasic**, because it can accept two protons in a reaction with a strong acid to become carbonic acid (water and carbon dioxide).

When reacted with hydrochloric acid, carbonate goes through a two stage reaction.

First, carbonate reacts with hydronium to produce hydrogen carbonate and water.

$$CO_3^{2-}{}_{(aq)} + H_3O^+{}_{(aq)} \rightarrow H_2O_{(l)} + HCO_3^-{}_{(aq)}$$

Further addition of hydrochloric acid results in the reaction of hydrogen carbonate with hydronium.

$$HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)} \rightarrow H_2O_{(l)} + H_2CO_{3\,(aq)}$$

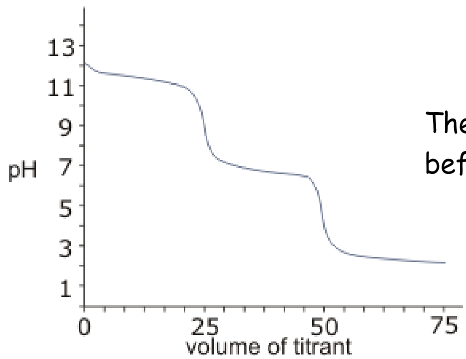
The sum of these reactions is:

$$CO_3^{2-}{}_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + HCO_3^-{}_{(aq)}$$

$$HCO_3^-{}_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + H_2CO_3{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + 2\,H_3O^+_{(aq)} \rightarrow 2\,H_2O_{(l)} + H_2CO_3{}_{(aq)}$$

The titration curve for a dibasic species and a strong acid looks like this:



The first reaction goes to completion before the second reaction begins

<u>Polyprotic Species</u>

A polyprotic species is an acid that <u>can donate more than one proton</u>

Terminology: HCl is monoprotic (1 proton)
H_2SO_4 is diprotic (2 protons)
H_3PO_4 is triprotic (3 protons)

Consider this reaction with sulfuric acid (diprotic):

(1) $H_2SO_4{}_{(aq)} + OH^-_{(aq)} \rightarrow HSO_4^-{}_{(aq)} + H_2O_{(l)}$

(2) $HSO_4^-{}_{(aq)} + OH^-_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + H_2O_{(l)}$

(3) $H_2SO_4{}_{(aq)} + 2\,OH^-_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + 2\,H_2O_{(l)}$

Unlike sulfuric acid, most polyprotic acids are weak acids.

Sample Problem

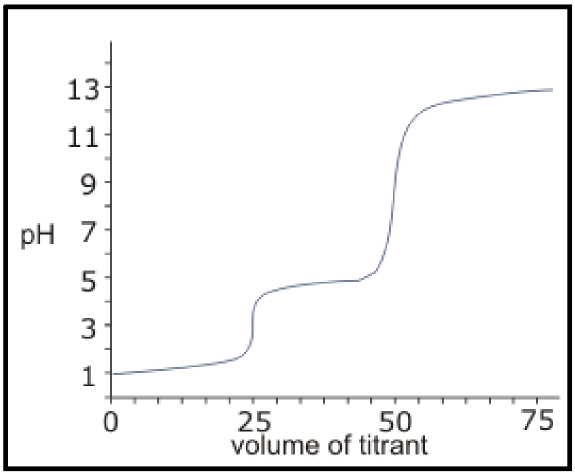
Write the reaction steps and the net equation for the quantitative reaction between oxalic acid and excess hydroxide ions.

Remove the first proton:

Remove the second proton:

Put the two reactions together to get the overall reaction:

The titration curve for the equation in the previous example would look like this:



- The pH is initially very low (sample is an acid).
- As hydroxide ions are added to the solution, a proton is removed each oxalic acid molecule.
- Just as the last few oxalic acid molecules react, the pH rises sharply (1st eqquivalence point).
- Then the added hydroxide ions react with hydrogen oxalate.
- The second equivalence point occurs when all of the hydrogen oxalate molecules have reacted.

To choose indicators for this titration, you must look for TWO indicators that change colour in the pH range that matches the equivalence points of the titration curve.