Types of titrations

There are many types of titrations with different procedures and goals. The most common types of qualitative titration are acid–base titrations and redox titrations.

1- Acid–base titration

Neutralization titrations are widely used to determine the amounts of acids and bases and to monitor the progress of reactions that produce or consume hydrogen ions. In addition, we investigate titration curves that are plots of pH vs. volume of titrant, and present several examples of pH calculations.

Acid–base titrations depend on the neutralization between an acid and a base when mixed in solution. In addition to the sample, an appropriate pH indicator is added to the titration chamber, reflecting the pH range of the equivalence point. The acid–base indicator indicates the endpoint of the titration by changing color. The endpoint and the equivalence point are not exactly the same because the equivalence point is determined by the stoichiometry of the reaction while the endpoint is just the color change from the indicator. Thus, a careful selection of the indicator will reduce the indicator error. For example, if the equivalence point is at a pH of 8.4, then the Phenolphthalein indicator would be used instead of Alizarin Yellow because phenolphthalein would reduce the indicator error. Common indicators, their colors, and the pH range in which they change color are given in the table above.[23] When more precise results are required, or when the reagents are a weak acid and a weak base, a pH meter or a conductance meter are used.

For very strong bases, such as organolithium reagent, metal amides, and hydrides, water is generally not a suitable solvent and indicators whose pKa are in the range of aqueous pH changes are of little use. Instead, the titrant and indicator used are much weaker acids, and anhydrous solvents such as THF are used.

The approximate pH during titration can be approximated by three kinds of calculations. Before beginning of titration, the concentration of is calculated in aqueous solution of weak acid before adding any base. When the number of moles of bases added equals the number of moles of initial acid or so called equivalence point, one of hydrolysis and the pH is calculated in the same way that the conjugate bases of the acid titrated was calculated. Between starting and end points, is obtained from the Henderson-Hasselbalch equation and titration mixture is considered as buffer. In Henderson-Hasselbalch equation the [acid] and [base] are said to be the molarities that would have been present even with dissociation or hydrolysis. In a buffer, can be exactly calculated but the dissociation of HA, the hydrolysis of and self-ionization of water must be taken into account. Four independent equations must be used:

In the equations, and are the moles of acid (HA) and salt (XA where X is the cation), respectively, used in the buffer, and the volume of solution is V. The law of mass action is applied to the ionization of water and the dissociation of acid to derive the first and second equations. The mass balance is used in the third equation, where the sum of and must equal to the number of moles of dissolved acid and base, respectively. Charge balance is used in the fourth equation, where the left hand side represents the total charge of the cations and the right hand side represents the total charge of the anions: is the molarity of the cation (e.g. sodium, if sodium salt of the acid or sodium hydroxide is used in making the buffer).

A Solutions and indicators for acid/base titrations Neutralization titrations depend on a chemical reaction of the analyte with a standard reagent. There are several different types of acid/base titrations.

1- The titration of a strong acid, such as hydrochloric or sulfuric acid, with a strong base, such as sodium hydroxide.
2- The titration of a weak acid, such as acetic or lactic acid, with a strong base.
3- The titration of a weak base, such as sodium cyanide or sodium salicylate, with a strong acid.

In all titrations, we must have a method of determining the point of chemical equivalence.

Typically, a chemical indicator or an instrumental method is used to locate the end point, which we hope is very close to the equivalence point. Our discussion focuses on the types of standard solutions and the chemical indicators that are used for neutralization titr. ns Standard Solutions The standard reagents used in acid/base titrations are always strong acids or strong bases, such as HCl, HClO4 , H_2SO_4 , NaOH, and KOH. Weak acids and bases are never used as standard reagents because they react incompletely with analytes. ¬ Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid. ¬ Nitric acid is seldom used because its oxidizing properties offer the potential for undesirable side reactions. Hot concentrated perchloric and sulfuric acids are potent oxidizing agents and are very hazardous. Acid/Base Indicators An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form. For example, the behavior of an acid-type indicator,

$HIn: HIn + H_2O \Leftrightarrow In^- + H_3O^+$

The equilibrium for a base-type indicator, In: $In + H_2O \Leftrightarrow InH^+ + OH$ base color acid color

The equilibrium-constant expression for the dissociation of an acid-type indicator is $K_a = [H_3O^+][In^-]$

Rearranging leads to $[H_3O^+] = Ka . [HIn] [HIn] [In^-]$

We see then that the hydronium ion is proportional to the ratio of the concentration of the acid form to the concentration of the base form of the indicator, which in turn controls the color of the solution.

Acid base Titration curves

A titration curve is a curve in the plane whose x-coordinates are the volume of titrant added since the beginning of the titration, and whose y-coordinate is the concentration of the analyte at the corresponding stage of the titration (in an acid–base titration, the y-coordinate is usually the pH of the solution).

In an acid–base titration, the titration curve reflects the strength of the corresponding acid and base. For a strong acid and a strong base, the curve will be relatively smooth and very steep near the equivalence point. Because of this, a small change in titrant volume near the equivalence point results in a large pH change and many indicators would be appropriate (for instance litmus, phenolphthalein or bromothymol blue).

If one reagent is a weak acid or base and the other is a strong acid or base, the titration curve is irregular and the pH shifts less with small additions of titrant near the equivalence point. For example, the titration curve for the titration between oxalic acid (a weak acid) and sodium hydroxide (a strong base) is pictured. The equivalence point occurs between pH 8-10, indicating the solution is basic at the equivalence point and an indicator such as phenolphthalein would be appropriate. Titration curves corresponding to weak bases and strong acids are similarly behaved, with the solution being acidic at the equivalence point and indicators such as methyl orange and bromothymol blue being most appropriate.

Titrations between a weak acid and a weak base have titration curves which are highly irregular. Because of this, no definite indicator may be appropriate and a pH meter is often used to monitor the reaction.

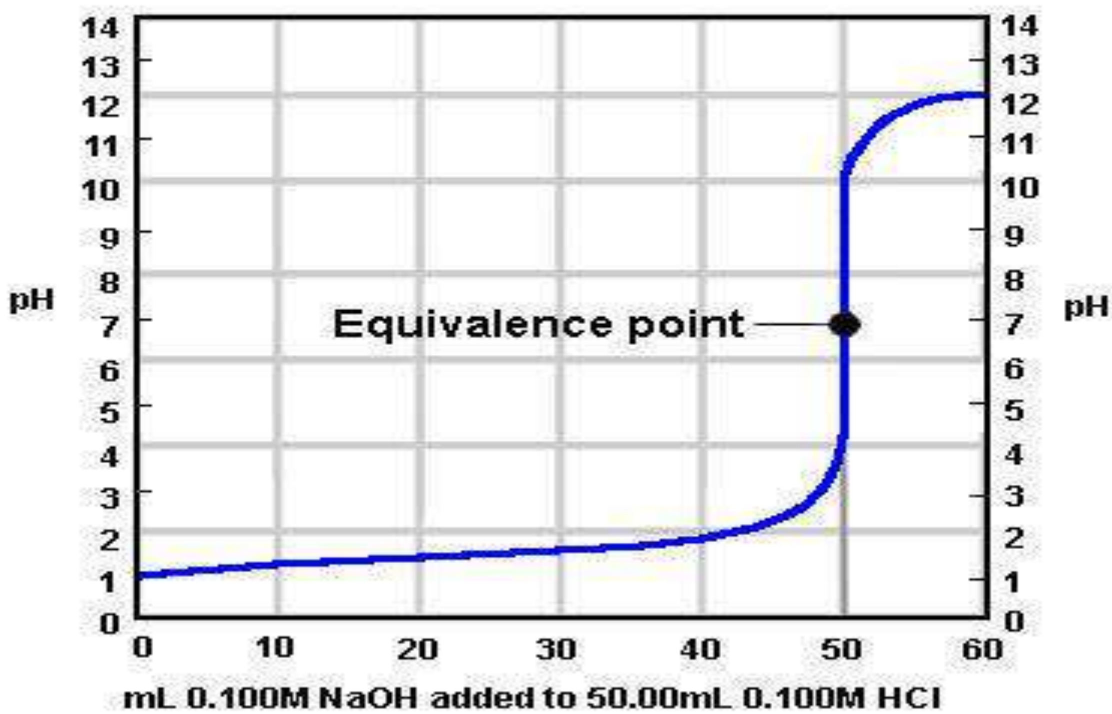
The type of function that can be used to describe the curve is called a sigmoid function.

A titration is a procedure for carrying out a chemical reaction between two solutions by the controlled addition from a buret of one solution (the titrant) to the other, allowing measurements to be made throughout the reaction. For a reaction between an acid and a base, a titration is useful for measuring the pH at various points throughout the reaction.

A titration curve is a graph of the pH as a function of the amount of titrant (acid or base) added.

1- Strong Acid-Strong Base Titrations

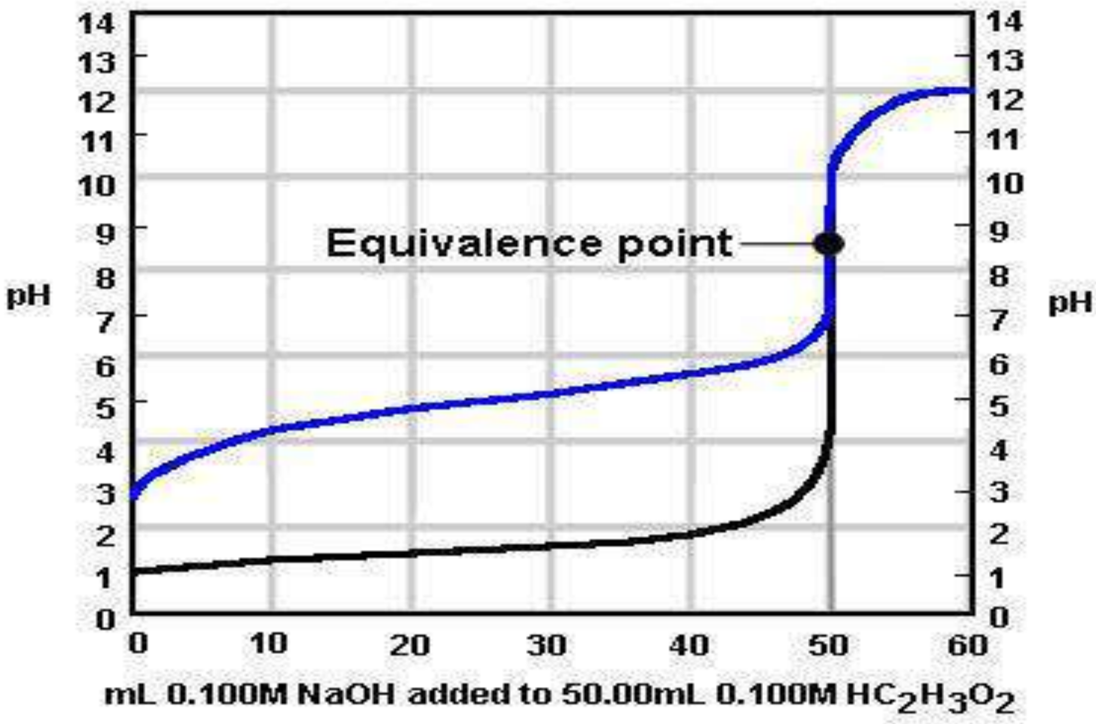
Here is an example of a titration curve, produced when a strong base is added to a strong acid. This curve shows how pH varies as 0.100 M NaOH is added to 50.0 mL of 0.100 M HCl.



The **equivalence point** of the titration is the point at which exactly enough titrant has been added to react with all of the substance being titrated with no titrant left over. In other words, at the equivalence point, the number of moles of titrant added so far corresponds exactly to the number of moles of substance being titrated according to the reaction stoichiometry. (In an acid-base titration, there is a 1:1 acid:base stoichiometry, so the equivalence point is the point where the moles of titrant added equals the moles of substance initially in the solution being titrated.)

2- Titrations Involving a Weak Acid or Weak Base

Titration curve of a weak acid being titrated by a strong base:



Here, 0.100 M NaOH is being added to 50.0 mL of 0.100 M acetic acid.

There are three major differences between this curve (in blue) and the one we saw before (in black):

1- The weak-acid solution has a higher initial pH.

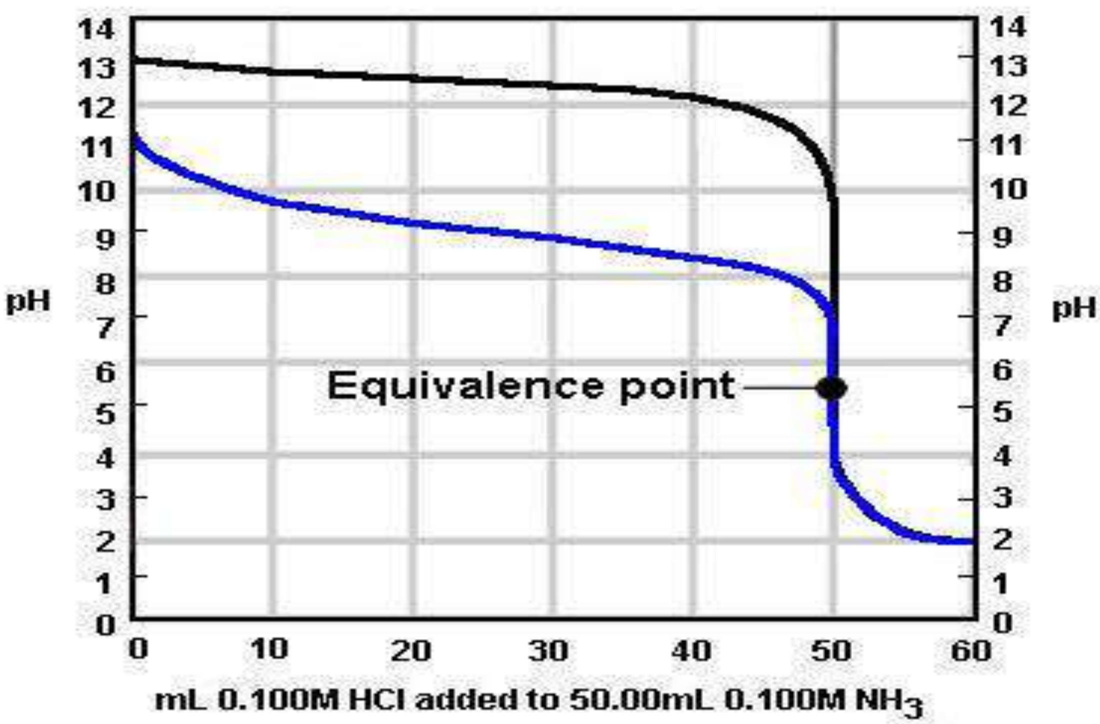
2- The pH rises more rapidly at the start, but less rapidly near the equivalence point.

3- The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS : The equivalence point for a weak acid-strong base titration has a pH > 7.00.

For a strong acid-weak base or weak acid-strong base titration, the pH will change rapidly at the very beginning and then have a gradual slope until near the equivalence point. The gradual slope results from a buffer solution being produced by the addition of the strong acid or base, which resists rapid change in pH until the added acid or base exceeds the buffer's capacity and the rapid pH change occurs near the equivalence point.

Titration curve of a weak base being titrated by a strong acid:



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As in the weak acid-strong base titration, there are three major differences between this curve (in blue) and a strong base-strong acid one (in black): (Note that the strong base-strong acid titration curve is identical to the strong acid-strong base titration, but flipped vertically.)

1- The weak-acid solution has a lower initial pH.
2- The pH drops more rapidly at the start, but less rapidly near the equivalence point.
3- The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS: The equivalence point for a weak base-strong acid titration has a pH < 7.00.

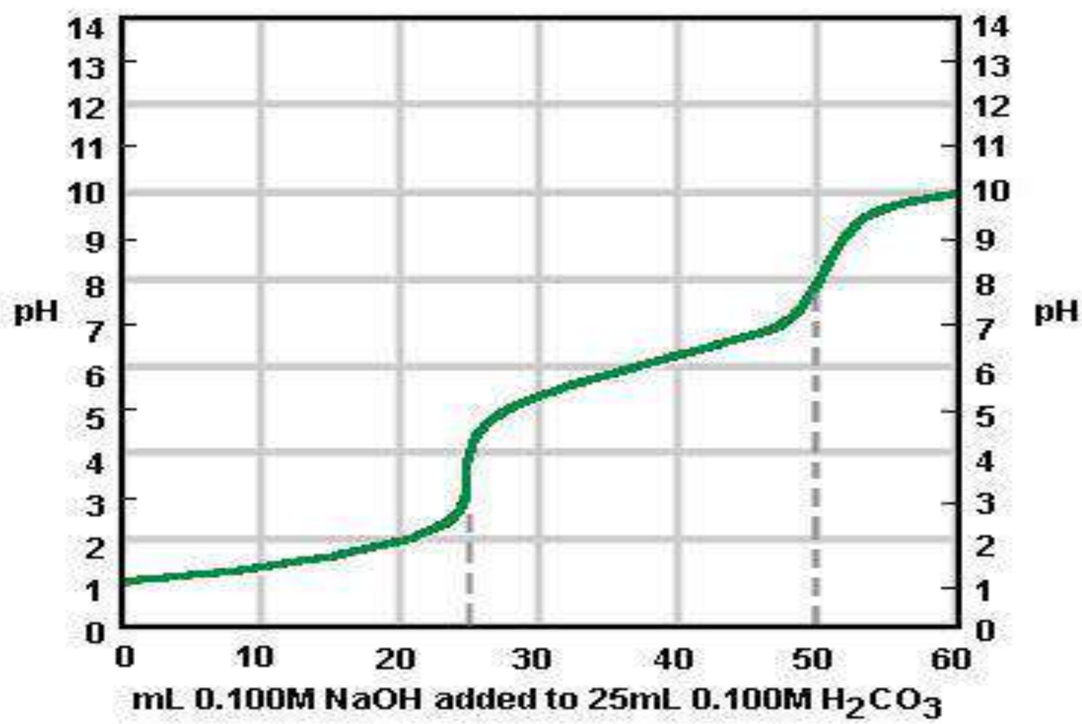
3- Titrations of Polyprotic Acids

An example of a polyprotic acid is H_2CO_3 which neutralizes in two steps:

H_2CO_3 (aq) + OH^- (aq) $\longrightarrow$ H_2O (l) + HCO_3^- (aq)

HCO_3^- (aq) + OH^- (aq) $\longrightarrow$ H_2O (l) + CO_3^{2-} (aq)

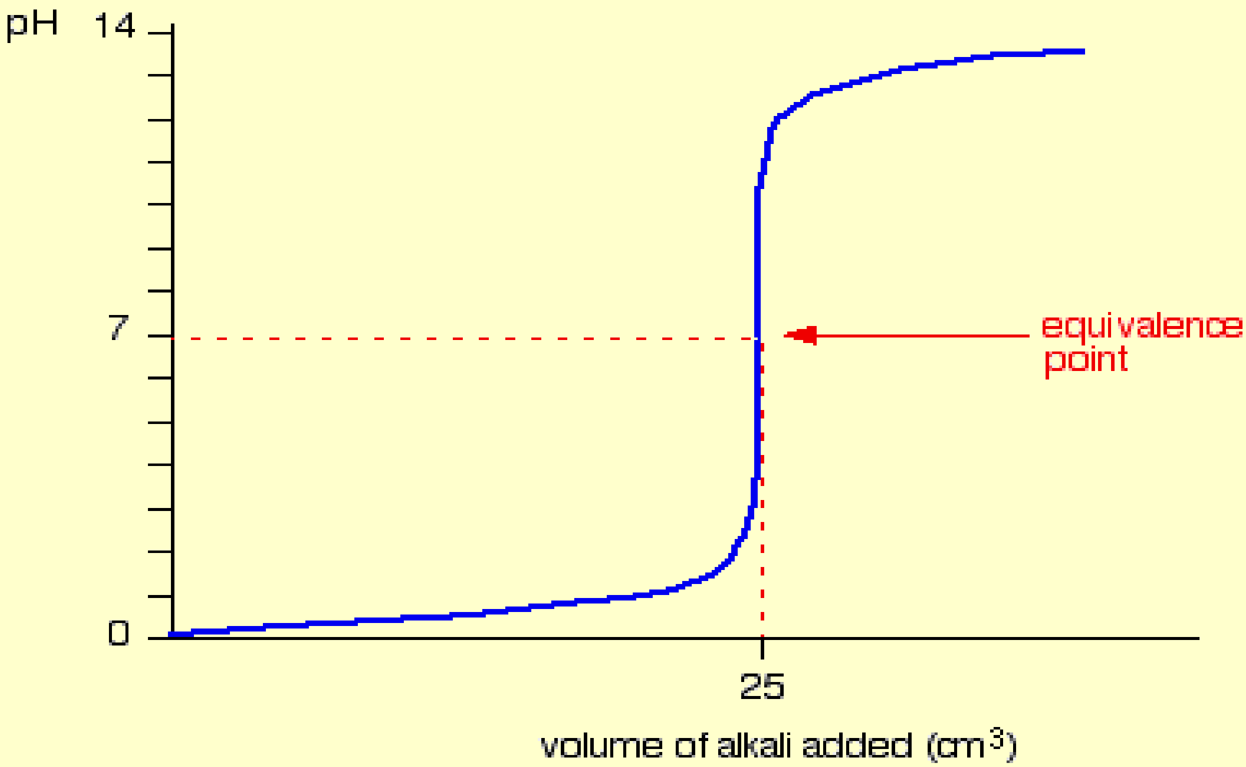
The titration curve for these reactions will look like this, with two equivalence points.



pH (TITRATION) CURVES

1- Strong acid and strong base

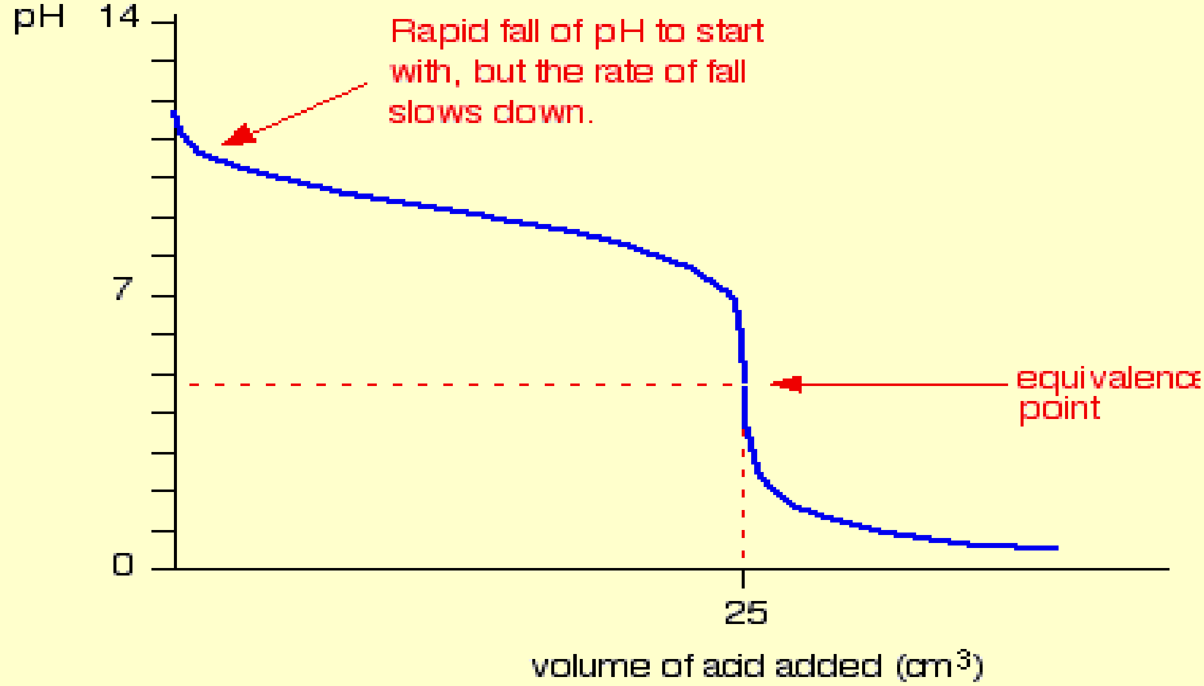
$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

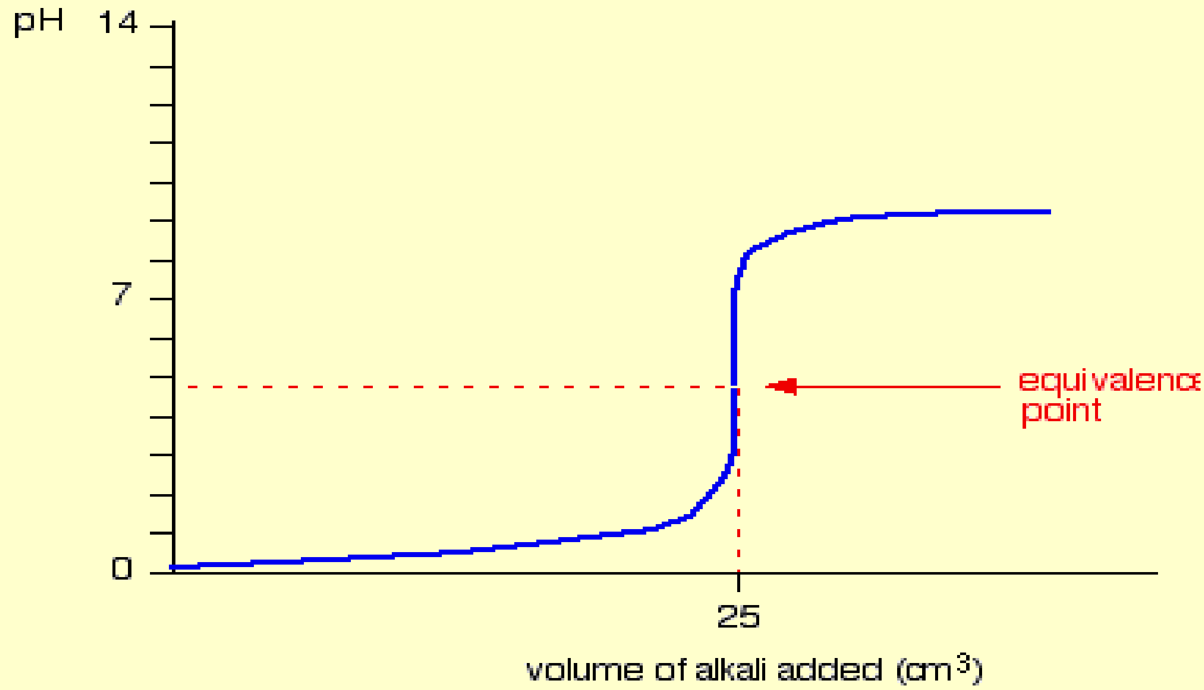


2- Titration curves for strong acid vs. weak base

This time we are going to use hydrochloric acid as the strong acid and ammonia solution as the weak base.

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$$

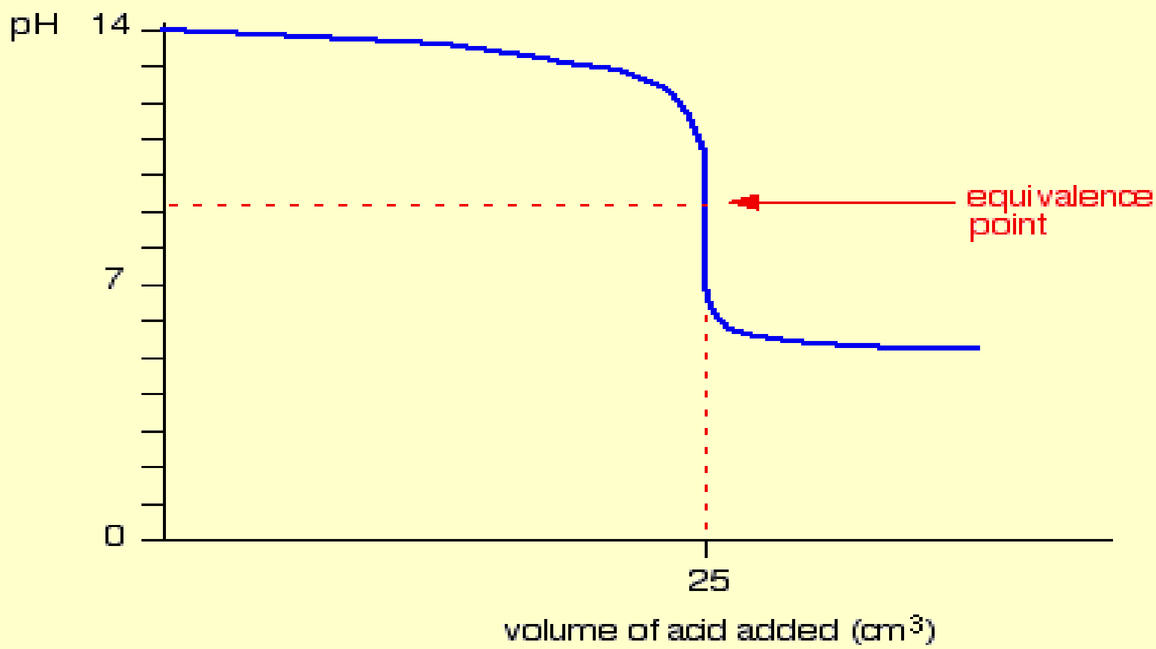


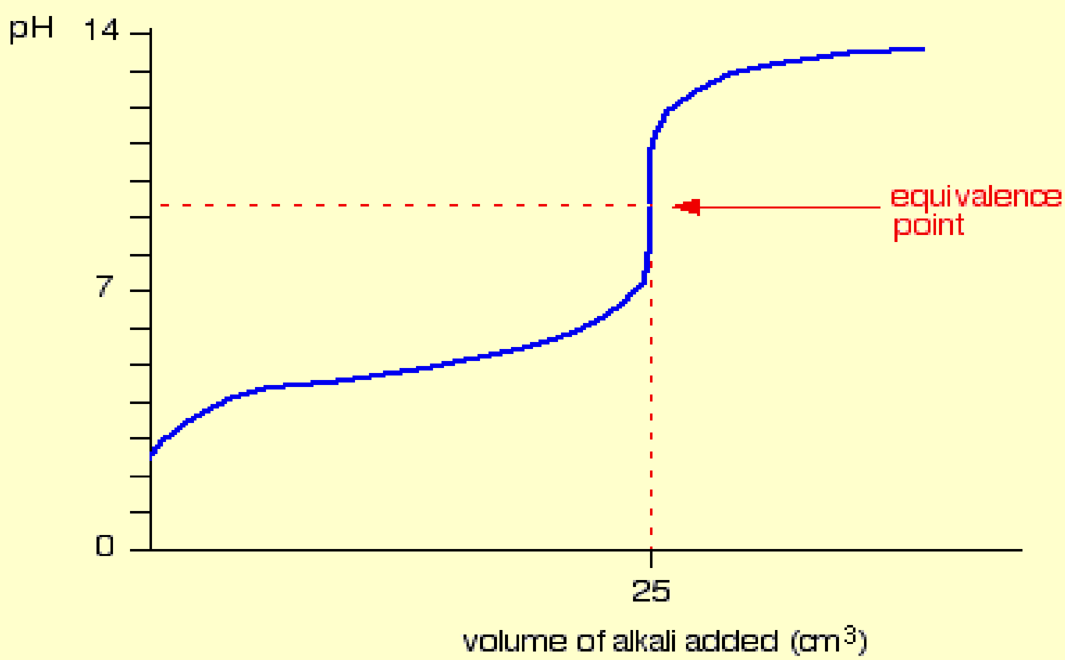


3- **Titration curves for weak acid vs. strong base**

We'll take ethanoic acid and sodium hydroxide as typical of a weak acid and a strong base.

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$$





4- **Titration curves for weak acid v weak base**

The common example of this would be ethanoic acid and ammonia.

$$CH_3COOH_{(aq)} + NH_{3(aq)} \longrightarrow CH_3COONH_{4(aq)}$$