

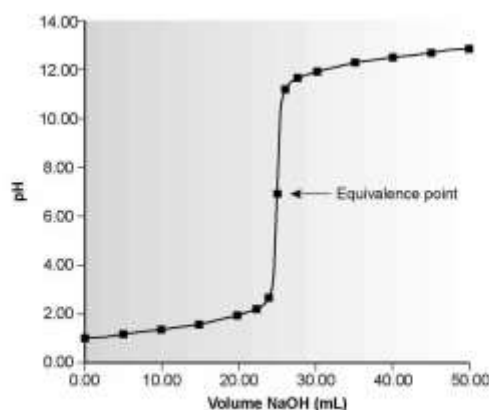
Classification of reaction in titrimetric analysis

The reaction employed in titrimetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation-reduction reactions, involves a change of oxidation state or, expressed another, a transfer of electron.

- 1- **Neutralization reaction**, or acidimetry and alkalimetry. These include the titration of free bases, or those formed from salts of weak acids by hydrolysis with a standard acid (acidimetry), and the titration of free acids, or those formed by the hydrolysis of salts or weak bases, with a standard base (alkalimetry). The reaction involves the combination of hydrogen and hydroxide ions to form water. Also, under this heading must be included titrations in non-aqueous solvents, most of which involve organic compounds.
- 2- **Precipitation reaction**. These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with solution of chloride. No change in oxidation state occurs.
- 3- **Complex formation reaction**. These depend upon the combination of ions, other than hydrogen or hydroxide ion, to form a soluble slightly dissociated ion or compound, as in the titration of a solution of a cyanide with silver nitrate. Ethylenediaminetetra-acetic acid, largely as the disodium salt of EDTA, is a very important reagent for complex formation titration and has become one of the most important reagents used in titrimetric analysis.
- 4- **Oxidation-reduction reaction**. Under this heading are included all reactions involving change in oxidation number or transfer of electrons among the reactive substance. The standard solutions are either oxidizing or reducing agents

Titration Curves

To find the end point we monitor some property of the titration reaction that has a well-defined value at the equivalence point. For example, the equivalence point for a titration of HCl with NaOH occurs at a pH of 7.0. We can find the end point, therefore, by monitoring the pH with a pH electrode or by adding an indicator that changes color at a pH of 7.0.



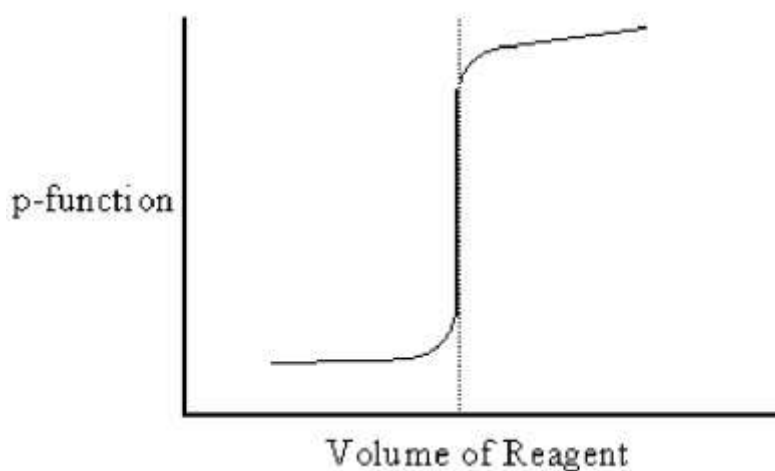
Acid-base titration curve for 25.0 mL of 0.100 M HCl with 0.100 M NaOH.

Suppose that the only available indicator changes color at a pH of 6.8. Is this end point close enough to the equivalence point that the titration error may be safely ignored? To answer this question, we need to know how the pH changes during the titration.

A titration curve provides us with a visual picture of how a property, such as pH, changes as we add titrant. We can measure this titration curve experimentally by suspending a pH electrode in the solution containing the analyte, monitoring the pH as titrant is added. We can also calculate the expected titration curve by considering the reactions responsible for the change in pH. However we arrive at the titration curve, we may use it to evaluate an indicator's likely titration error. For example, the titration curve in the above figure shows us that an end point pH of 6.8 produces a small titration error. Stopping the titration at an end point pH of 11.6, on the other hand, gives an unacceptably large titration error. A titration curve is a plot of reagent volume added versus some function of the analyte concentration. Volume of added reagent is generally plotted on the x axis. The measured parameter that is a function of analyte concentration is plotted on the y axis.

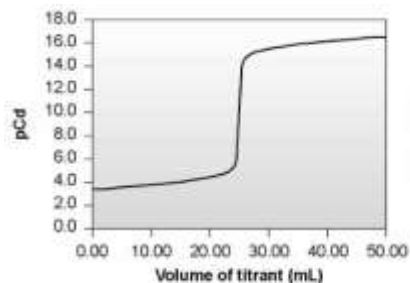
Two general titration curve types are seen:

1. Sigmoidal curve - a "z" or "s"-shaped curve where the y axis is a p-function of the analyte (or the reagent reacted with the analyte during titration) or the potential of an ion-specific electrode.

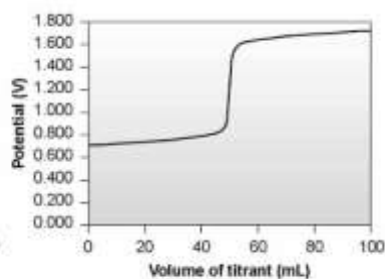


The equivalent point is observed in the middle of the "middle" segment of the "z" or "s."

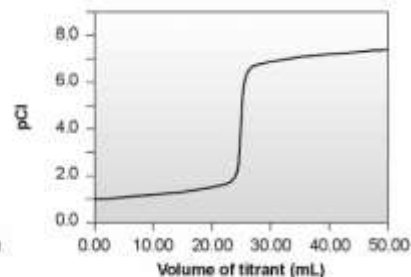
Examples of Sigmoidal titration curves.



Complexation titration



Redox titration



Precipitation titration.

2. Linear-segment curve - a curve generally consisting of two-line segments that intersect at an angle.

