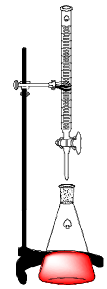
Titrimetry

This brief tutorial describes the basic procedure for conducting a titration in the Chem 260 lab. Although the tutorial makes use of acid–base chemistry, the discussion also applies to other types of reactions.

What is an Acid–Base Titration?
An acid–base titration is an technique in which a solution containing an acid (or a base) is added dropwise to a solution containing a base (or an acid). The solution added dropwise is called the titrant and the solution to which the titrant is added is called the sample. The sample is normally placed in an Erlenmeyer flask whose size is sufficient to contain both the sample and the added titrant, with sufficient room to swirl the solution without having it slosh out of the flask. The titrant is placed in a buret allowing for its controlled addition to the sample. The figure to the right shows a typical setup.



How is a Titration Used to Determine the Concentration of an Acid or Base?
Suppose, for example, that we have a monoprotic acid, HA, of unknown concentration and a monoprotic base, B, whose concentration is known. When mixed together, the acid and base react according to the following stoichiometry

$$\mathrm{HA}(aq) + \mathrm{B}(aq) \rightarrow \mathrm{HB}^{+}(aq) + \mathrm{A}^{-}(aq)$$

Let's assume, as well, that the reaction essentially proceeds to completion. If we titrate a solution of HA using B as a titrant until they mix in an exact stoichiometric ratio, then we know that

$$\text{moles B} = \text{moles HA}$$

because the reaction's stoichiometry is 1:1. The moles of HA and the moles of B are equal to the product of their respective molarities, M, and volumes, V

$$\text{moles HA} = M_{\mathrm{HA}} \times V_{\mathrm{HA}}$$

$$\text{moles B} = M_{\mathrm{B}} \times V_{\mathrm{B}}$$

Substituting back leaves us with

$$M_{\mathrm{B}} \times V_{\mathrm{B}} = M_{\mathrm{HA}} \times V_{\mathrm{HA}}$$

As an example, if 36.42 mL of a 0.116 M solution of B completely reacts with 25.00 mL of HA, then the concentration of HA is

$$M_{\mathrm{HA}} = \frac{M_{\mathrm{B}} \times V_{\mathrm{B}}}{V_{\mathrm{HA}}} = \frac{(0.116\ \mathrm{M})(36.42\ \mathrm{ml})}{25.00\ \mathrm{mL}} = 0.169\ \mathrm{M\ HA}$$

If the acid is diprotic, H_2A, and we react it with sufficient B such that both protons are completely consumed, then

$$\mathrm{H_2A}(aq) + 2\mathrm{B}(aq) \rightarrow 2\mathrm{HB}^{+}(aq) + \mathrm{A}^{2-}(aq)$$

and

$$M_{\mathrm{B}} \times V_{\mathrm{B}} = 2 \times M_{\mathrm{H_2A}} \times V_{\mathrm{H_2A}}$$

Obviously, there are many other possibilities (diprotic bases, triprotic acids, etc.), but the details for such cases follow easily from this description.

Sometimes the acid or base is obtained as a solid. Suppose, for example, you need to determine the concentration of a monobasic strong base, B, by titrating it against a known mass of a solid monoprotic weak acid, HA. In this case we obtain the concentration of the base using the following equation

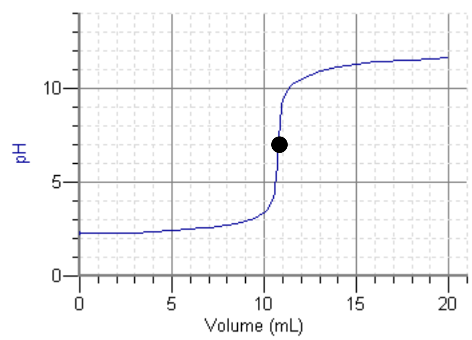
$$\text{moles B} = \text{moles HA}$$

$$M_B \times V_B = \text{g HA}/MM_{HA}$$

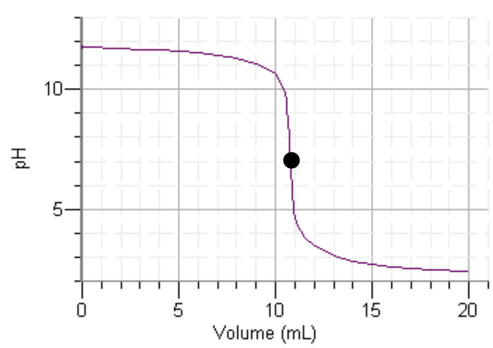
where MM_{HA} is the molar mass of HA.

How Do We Know When an Acid and Base Have Been Mixed Stoichiometrically?

When the titrant and sample are mixed in an exact stoichiometric ratio the titration is said to have reached its equivalence point. Finding this equivalence point is the key to any titration. There are two general approaches for finding the equivalence point: (1) using a visual indicator that changes color at the equivalence point, or (2) measuring the sample's pH as the titrant is added. The use of an indicator is straightforward and needs no detailed discussion (you just add the titrant dropwise until the indicator changes color, recording the total amount of titrant needed to reach the equivalence point).[1]



Suppose the sample is a strong acid and the titrant is a strong base. Before adding titrant the sample's pH depends on the strong acid's concentration. Adding titrant causes a slow increase in pH as the strong base neutralizes the strong acid. The rate at which the pH changes becomes greater as we near the equivalence point, reaching its maximum rate of change at the equivalence point, which in this case occurs when the pH is 7.00. Following the equivalence point, the rate of change in pH becomes smaller, producing a slow, gradual rise in pH. The resulting titration curve looks something like the figure shown to the right where the equivalence point is shown by the dot (●).



The titration curves for other samples are similar in shape. When the sample is a strong base and the titrant is a strong acid, for example, ten the titration curve begins at a more basic pH and ends at a more acidic pH; the general shape, as shown to the left, is the same. Note that the equivalence point in this case also occurs at a pH of 7.00.

Although the equivalence points in these two examples are both 7.00, this is not always the case. When titrating a weak acid, HA, with a strong base, for example, the pH at the equivalence point is basic because the reaction

$$HA(aq) + OH^-(aq) \rightarrow H_2O(aq) + A^-(aq)$$

[1] To be exact, a visual indicator signals an *endpoint,* not an equivalence point. If the proper indicator is chosen, then the difference between the endpoint and the equivalence point is inconsequential. Selecting an appropriate indicator is a topic that we will not explore in this course.

produces a solution of the weak acid's conjugate weak base, A^-, at the equivalence point. The pH, therefore, is greater than 7.00. Titrating a weak base with a strong acid, of course, gives an equivalence point that is less than 7.00.

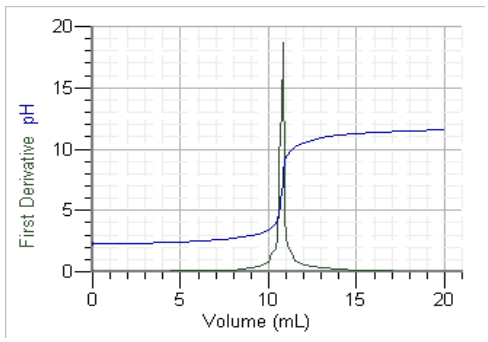
Automated Titrations

The most common equipment for a titration is a manual buret in which the analyst (that's you!) opens and closes the stopcock, recording the pH after each addition of titrant. This is time-consuming and tedious. A more convenient method for recording a titration curve is to use an automated titrator that records both the volume of titrant added and the pH as a function of time. In this case the titrant is allowed to stream into the sample, usually at a slow rate, and the pH monitored continuously. In the Chem 260 lab this is accomplished using the Vernier Drop Counter. Further details on their use is available on the course's website.

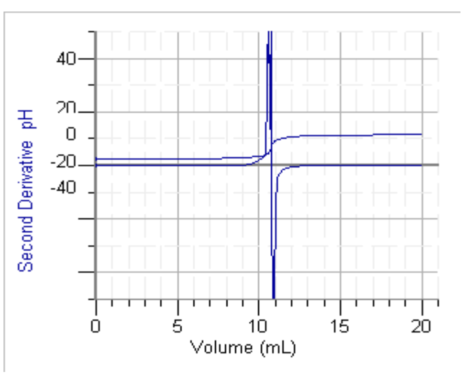
Processing Titration Data to Better Locate the Equivalence Point

Generally, the limiting factor in using the data from a titration curve is the accuracy and precision of locating the equivalence point. Determining the equivalence point by a visual inspection of the titration curve, which is the most common method, can be tricky if the rate of change in pH near the equivalence point is not very large. Another approach, which sometimes overcomes this limitation, is to plot the titration curve's first-derivative; that is, to plot $d\text{pH}/dV_{\text{titrant}}$ on the y-axis versus the volume of titrant on the x-axis.

This works because the first-derivative of a curve at any given point is the slope of the curve at that point. Because the equivalence point is where the rate of change in pH is greatest, the first-derivative has its most positive (or its most negative) value at the equivalence point. For example, when titrating a strong acid with a strong base, the titration curve and its first-derivative look like the figure shown on the right; note that the normal titration curve is shown for comparison.



Alternatively, one can plot the titration curve's second-derivative, for the which the equivalence point is marked by the derivative's crossing of the volume axis (see figure below; again, the normal titration curve is shown for comparison).



One limitation to derivative techniques is that they enhance noise (random variations in pH not related to the addition of titrant) more dramatically than they enhance the analytical signal (the change in pH due to the addition of titrant). This can make derivative titration curves, particularly second-derivative titration curves, difficult to interpret.

Titrations Based on Other Types of Reactions

Although this tutorial uses acid–base reactions to explain titrimetry, any chemical reaction can serve as the basis of a titration provided that the reaction is favorable, that it occurs rapidly, and that there is a suitable means for determining the equivalence point. The shape of such titration curves are similar to an acid–base titration curve.