Titration

Titration setup: the titrant drops from the burette into the analyte solution in the flask. An indicator present then changes color at the endpoint.

Titration is a common laboratory method of quantitative/chemical analysis which can be used to determine the concentration of a known reactant. Because volume measurements play a key role in titration, it is also known as *volumetric analysis*. A reagent, called the *titrant*, of known concentration (a standard solution) and volume is used to react with a measured quantity of reactant (Analyte). Using a calibrated burette to add the titrant, it is possible to determine the exact amount that has been consumed when the *endpoint* is reached. The endpoint is the point at which the titration is stopped. This is classically a point at which the number of moles of titrant is equal to the number of moles of analyte, or some multiple thereof (as in di- or tri- protic acids). In the classic strong acid-strong base titration the endpoint of a titration is when the pH of the reactant is just about equal to 7, and often when the solution permanently changes color due to an indicator. There are however many different types of titrations (see below).

Many methods can be used to indicate the endpoint of a reaction; titrations often use visual indicators (the reactant mixture changes colour). In simple acid-base titrations a pH indicator may be used, such as phenolphthalein, which turns (and stays) pink when a certain pH is reached or exceeded. Methyl orange can also be used, which is red in acids and yellow in alkalis.

Not every titration requires an indicator. In some cases, either the reactants or the products are strongly coloured and can serve as the "indicator". For example, an oxidation-reduction titration using potassium permanganate (pink/purple) as the titrant does not require an indicator. When the titrant is reduced, it turns colourless. After the equivalence point, there is excess titrant present. The equivalence point is identified from the first faint pink colour that persists in the solution being titrated.

Due to the logarithmic nature of the pH curve, the transitions are generally extremely sharp, and thus a single drop of titrant just before the *endpoint* can change the pH significantly — leading to an immediate colour change in the indicator. That said, there is a slight difference between the change in indicator color and the actual equivalence point of the titration. This error is referred to as an indicator error, and it is indeterminate.

Preparing a sample for titration

In a titration, both titrant and analyte are required to be aqueous, or in a solution form. If the sample isn't a liquid or solution, the samples must be dissolved. If the analyte is very concentrated in the sample, it might be useful to dilute the sample.

Although the vast majority of titrations are carried out in aqueous solution, other solvents such as glacial acetic acid or ethanol (in petrochemistry) are used for special purposes.

A measured amount of the sample can be given in the flask and then be dissolved or diluted. The mathematical result of the titration can be calculated directly with the measured amount. Sometimes the sample is dissolved or diluted beforehand and a measured amount of the solution is used for titration. In this case the dissolving or diluting must be done accurately with a known coefficient because the mathematical result of the titration must be multiplied with this factor.

A lot of titrations require buffering to maintain a certain pH for the reaction. Therefore buffer solutions are added to the reactant solution in the flask.

Some titrations require "masking" of a certain ion. This can be necessary when two reactants in the sample would react with the titrant and only one of them must be analysed, or when the reaction would be disturbed or inhibited by this ion. In this case another solution is added to the sample which "masks" the unwanted ion (for instance by a weak binding with it or even forming a solid insoluble substance with it).

Some redox reactions may require heating the solution with the sample and titration while the solution is still hot (to increase the reaction rate).

Procedure

N.B. Before starting, make sure that all of your glassware—especially the burette—is clean and dry. Alternatively, you can rinse out the glassware first with distilled water to remove as much impurities and dirt on the glassware as possible, then with the solution that is to be stored in the particular piece to coat the glassware with the solution so as to not affect the concentration of the solution.

1. Accurately measure a volume of the reactant (this is usually done with a graduated pipette) into a beaker or Erlenmeyer flask. (Precaution: When reading liquid level in any measuring apparatus, always take care to avoid parallax error by putting your eye level to the same level as the liquid, and read the bottom of the meniscus.)
2. Add a small amount of any suitable indicator to the flask. It is preferred to put no more than three drops of indicator, for too much indicator might affect the results.
3. Flush through the burette first with tap water, then distilled water and finally the titrant.
4. Pour the titrant into the burette, enlisting the help of a filter funnel, if necessary. Remove the filter funnel, if used. This is important as leftover solution from the funnel can continue flowing into the burette, affecting the reading.
5. IMPORTANT: Ensure that there is no air-space at the tip of the burette. This can be seen as a bubble in between the tap and the the end tip of the burette. (To remedy this, open the tap and allow a fast jet of solution to flow through, shaking the burette vigorously if necessary, collecting the titrant solution in a separate beaker as waste.)
6. Read and record the *start-point* of the liquid on the burette.
7. Turn the tap of the burette to allow the titrant to fall slowly into the analyte. For best results, ensure that the end tip of the burette is inside the flask or beaker (but not touching the solution!). Swirl the flask with the other hand or with a magnetic "flea".
8. The indicator should change colour as the titrant is added, but then quickly return to its original colour.
9. As the end-point is approached, the indicator takes longer to turn back to its starting colour. Add the titrant slowly at this point (one drop at a time).
10. When the indicator remains permanantly at its end colour, the reaction has reached the end point. Measure the amount of titrant liquid remaining, as shown on the scale of the burette. As is standard for measuring any liquids in the laboratory, measure from the bottom of the meniscus if it is concave, and from the top if it is convex. The volume used (endpoint volume) is the difference of the two readings (initial and final).
11. Repeat at least twice more, then take the average of the best volumes. (Best volumes are readings that fall within a certain range of each other. This range is usually ±0.2cm³)

Once the number of moles of reactant that have been neutralized has been determined, then it is easy to calculate the concentration, usually measured in moles per cubic decimetre (mol/dm³) or moles per litre (mol/*l*). Both these units are equal. (ie 0.1 mol/dm³ = 0.1 mol/*l*)

$$C_r = \frac{N_r}{V_r}$$

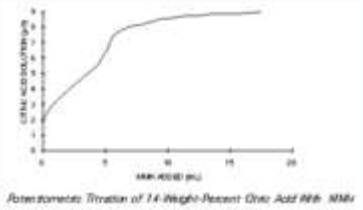
in the above formula

C represents the concentration (Molarity)

N represents the number of moles (mol), and

V represents the volume of the solution (L).

Titration curves



A typical titration curve. Citric acid is, however, triprotic - from visual inspection, the curve does not clearly show the first and third equivalence points, showing only the second equivalence point.

Titrations are often recorded on titration curves, whose compositions are generally identical: the independent variable is the volume of the titrant, while the dependent variable is the pH of the solution (which changes depending on the composition of the two solutions). The equivalence point is a significant point on the graph (the point at which all of the starting solution, usually an acid, has been neutralized by the titrant, usually a base). It can be calculated precisely by finding the second derivative of the titration curve and computing the points of inflection (where the graph changes concavity); however, in most cases, simple visual inspection of the curve will suffice (in the curve given to the right, the only immediately visible equivalence point (actually the second equivalence point) occurs after roughly 5 mL of MMH has been titrated with the citric acid solution) Therefore, to calculate the other two Pka values, one must take the seen pKa value and divide this volume into the respective amounts to find the 2 other equivalence points, and therefore half-equivalence points.

In monoprotic acids, the point halfway between the beginning of the curve (before any titrant has been added) and the equivalence point is significant: at that point, the concentrations of the two solutions (the titrant and the original solution) are equal. Therefore, the Henderson-Hasselbalch equation can be solved in this manner:

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$
$$pH = pK_a + \log(1)$$
$$pH = pK$$

Therefore, one can easily find the acid dissociation constant of the monoprotic acid by finding the pH of the point halfway between the beginning of the curve and the equivalence point, and solving the simplified equation. In the case of the sample curve, the K_a would be approximately $1.78 * 10^{-5}$ from visual inspection (the actual K_{a2} is $1.7 * 10^{-5}$).

For polyprotic acids, calculating the acid dissociation constants is only marginally more difficult: the first acid dissociation constant can be calculated the same way as it would be calculated in a monoprotic acid. The second acid dissociation constant, however, is the point halfway between the first equivalence point and the second equivalence point (and so on for acids that release more than two protons, such as phosphoric acid).

Types

Titrations can be classified by the type of reaction, or by the method used to determine the endpoint. In many cases, several different methods could be used to detect the endpoint of a given type of reaction.

By Reaction

Different types of titration reaction include:

- Acid-base titration is based on the neutralization reaction between the analyte and an acidic or basic titrant. These most commonly use a pH indicator, a pH meter, or a conductance meter to determine the endpoint.
- A Redox titration is based on an oxidation-reduction reaction between the analyte and titrant. These most commonly use a potentiometer or a redox indicator to determine the endpoint. Frequently either the reactants or the titrant have a colour intense enough that an additional indicator is not needed.
- A Complexometric titration is based on the formation of a complex between the analyte and the titrant. The chelating agent EDTA is very commonly used to titrate metal ions in solution. These titrations generally require specialized indicators that form weaker complexes with the analyte. A common example is Eriochrome Black T for the titration of calcium and magnesium ions.
- A form of titration can also be used to determine the concentration of a virus or bacterium. The original sample is diluted (in some fixed ratio, such as 1:1, 1:2, 1:4, 1:8, etc.) until the last dilution does not give a positive test for the presence of the virus. This value, the titre, may be based on TCID50, EID50, ELD50, LD50 or pfu. This procedure is more commonly known as an assay.

By Detection

Different methods to determine the endpoint include:

- pH indicator: This is a substance that changes colour in response to a chemical change. An acid-base indicator (e.g., phenolphthalein) changes colour depending on the pH. Redox indicators are also frequently used. A drop of indicator solution is added to the titration at the start; when the colour changes the endpoint has been reached.
- A potentiometer can also be used. This is an instrument which measures the electrode potential of the solution. These are used for titrations based on a redox reaction; the potential of the working electrode will suddenly change as the endpoint is reached.
- pH meter: This is a potentiometer which uses an electrode whose potential depends on the amount of H+ ion present in the solution. (This is an example of an ion selective electrode. This allows the pH of the solution to be measured throughout the titration. At the end point there will be a sudden change in the measured pH. It can be more accurate than the indicator method, and is very easily automated.

Other terms

The term back titration is used when a titration is done "backwards": instead of titrating the original analyte, one adds a known excess of a standard reagent to the solution, then titrates the excess. A back titration is useful if the end point of the reverse titration is easier to identify than the end point of the normal titration. They are also useful if the reaction between the analyte and the titrant is very slow.