Introduction to Analytical Chemistry

Introduction

Everything is made of chemicals. Analytical chemistry determine what and how much. In other words analytical chemistry is concerned with the separation, identification, and determination of the relative amounts of the components making up a sample.

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions what is it (qualitative) and how much is it (quantitative). Analytical chemistry answering for basic questions about a material sample:

- What?
- Where?
- How much?
- What arrangement, structure or form?

Applications of Analytical Chemistry

Analytical chemistry used in many fields:

- In ***medicine***, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.
- In ***industry***, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical. Many household products, fuels, paints, pharmaceuticals, etc. are analysed by the procedures developed by analytical chemists before being sold to the consumer.
- ***Enviermental quality*** is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.
- The nutritional value of ***food*** is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in a food are often calculated from the chemical analysis.
- ***Forensic analysis*** - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.
- ***Bioanalytical chemistry and analysis*** - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).

Applications of analytical chemistry in pharmacy sciences.

- Pharmaceutical chemistry.
- Pharmaceutical industry (quality control).
- Analytical toxicology is concerned with the detection, identification and measurement of drugs and other foreign compounds (and their metabolites in biological and related specimens.
- Natural products detection, isolation, and structural determination.

Steps in a Chemical Analysis

- Define the problem.
- Select a method.
- Sampling (obtain sample).
- Sample preparation (prepare sample for analysis).
- Perform any necessary chemical separations
- Analysis (perform the measurement).
- Calculate the results and report.

The Language of Analytical Chemistry

Qualitative analysis: An analysis in which we determine the identity of the constituent species in a sample.

Quantitative analysis: An analysis in which we determine how much of a constituent species is present in a sample.

Analytes: The constituents of interest in a sample.

Matrix: All other constituents in a sample except for the analytes.

A **selective reaction** or test is one that can occur with other substances but exhibits a degree of preference for the substance of interest.

A **specific reaction** or test is one that occurs only with the substance of interest.

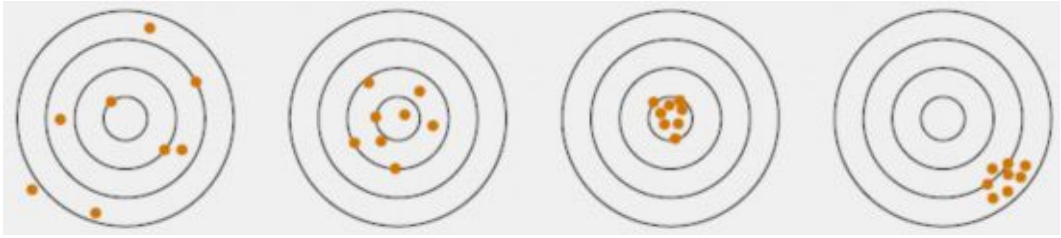
Note: few reactions are specific but many exhibit selectivity.

Detection limit: A statistical statement about the smallest amount of analyte that can be determined with confidence.

Precision and Accuracy

Precision describes the reproducibility of a result. If you measure a quantity several times and the values agree closely with one another, your measurement is precise. If the values vary widely, your measurement is not very precise.

Accuracy describes how close a measured value is to the "true" value. If a known standard is available, accuracy is how close your value is to the known value.



(neither precise nor accurate) (accurate but not precise) (accurate and precise) (precise but not accurate)

Classifying Analytical Techniques

Classical techniques

Mass, volume, and charge are the most common signals for classical techniques, and the corresponding techniques are:

1- Gravimetric techniques.
2- Volumetric techniques.
3- Coulometeric techniques.

Instrumental techniques

1- Spectroscopic methods - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

2- Electroanalytic methods - measure an electrical property (i.e., potential, current, resistance, amperes, etc.) chemically related to the amount of analyte.

Basic Tools and Operations of Analytical Chemistry

Basic Equipment

Measurements are made using appropriate equipment or instruments. The array of equipment and instrumentation used in analytical chemistry is impressive, ranging from the simple and inexpensive, to the complex and costly.

Equipments for Measuring Mass (Analytical Balance)

An object's mass is measured using a **balance.** The most common type of balance is an in which the balance pan is placed over an electromagnet. Another type of analytical balance is the ***mechanical balances*** which are replaced by the electronic balances.

electronic balance

electronic balance

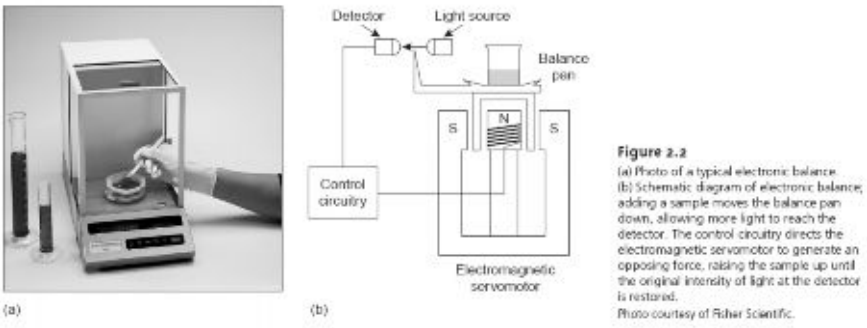


Figure 2.2
(a) Photo of a typical electronic balance. (b) Schematic diagram of electronic balance; adding a sample moves the balance pan down, allowing more light to reach the detector. The control circuitry directs the electromagnetic servomotor to generate an opposing force, raising the sample up until the original intensity of light at the detector is restored.
Photo courtesy of Fisher Scientific.

Equipment for Measuring Volume

Analytical chemists use a variety of glassware to measure volume. The type of glassware used depends on how exact the volume needs to be.

Volumetric flask is designed to contain a specified volume of solution at a stated temperature, usually 20 °C.

Pipette is used to deliver a specified volume of solution. Several different styles of pipets are available.

Figure 2.5
Common types of pipets and syringes: (a) transfer pipet; (b) measuring pipet; (c) digital pipet; (d) syringe.
Photos courtesy of Fisher Scientific.

Burette is volumetric glassware used to deliver variable, but known volumes of solution. A burette is a long, narrow tube with graduated markings, and a stopcock for dispensing the solution.

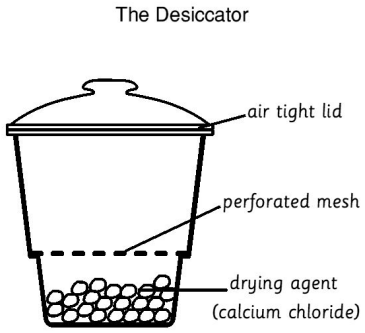
Equipment for Drying

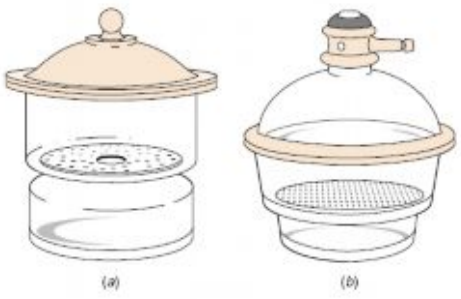
Reagents, precipitates, and glassware are conveniently dried in an oven at 110°C. Many materials need to be dried prior to their analysis to remove residual moisture. Depending on the material, heating to a temperature of 110–140 °C is usually sufficient. Other materials need to be heated to much higher temperatures to initiate thermal decomposition. Both processes can be accomplished using a ***laboratory oven*** capable of providing the required temperature. Commercial laboratory ovens are used when the maximum desired temperature is 160–325 °C (depending on the model). Higher temperatures, up to 1700° C, can be achieved using a muffle ***furnace***.

Conventional laboratory oven used for drying materials.

Example of a muffle furnace used for heating samples to maximum temperatures of 1100–1700 °C.

After drying or decomposing a sample, it should be cooled to room temperature in a desiccator to avoid the readsorption of moisture. A ***desiccator*** is a closed container that isolates the sample from the atmosphere. A drying agent, called a **desiccant,** is placed in the bottom of the container. Typical desiccants include calcium chloride and silica gel.

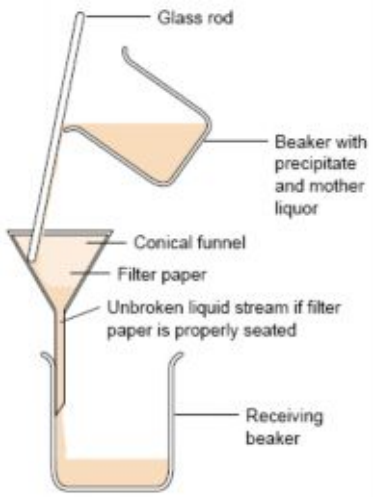




(a) Ordinary desiccator. (*b*) Vacuum desiccator

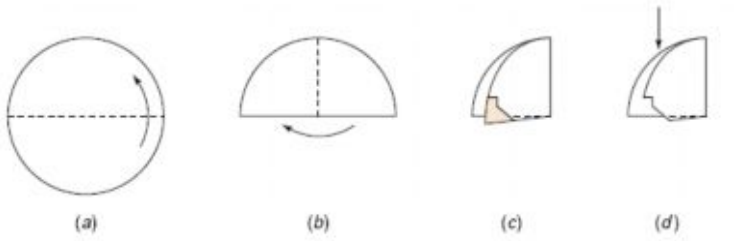
Filtration

In *gravimetric analysis*, the mass of product from a reaction is measured to determine how much unknown was present. Precipitates from gravimetric analyses are collected by filtration. Liquid from which a substance precipitates or crystallizes is called the **mother liquor**. Liquid that passes through the filter is called **filtrate**.



Filtering a precipitate.
The conical funnel is supported by a metal ring attached to a ring stand, neither of which is shown.

Folding filter paper for a conical funnel.
(*a*) Fold the paper in half.
(*b*) Then fold it in half again.
(*c*) Tear off a corner to allow better seating of the paper in the funnel.
(*d*) Open the side that was not torn when fitting the paper in the funnel.



Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. Two methods for preparing solutions are described in this section.

Preparing Stock Solutions

A ***stock solution*** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume.

Preparing Solutions by Dilution

Solutions with small concentrations are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume.

Volumetric Methods of Analysis
Titrimetric Analysis

Introduction

The term titrimetric analysis refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of a substance to be determined. The solution of accurately known concentration is called ***standard solution***.

The term volumetric analysis was used for this form of quantitative determination but it has now been replaced by titrimetric analysis. In titrimetric analysis the reagent of known concentration is called ***titrant*** and the substance being titrated is termed the ***titrand***.

The standard solution is usually add from a long graduated tube called burette. The process of adding the standard solution until the reaction is just complete is termed titration. The point at which this occurs is called ***equivalence point*** or the theoretical (or stoichiometric) end point. The completion of the titration is detected by some physical change, produced by the standard solution itself or, more usually, by the addition of an auxiliary reagent, known as an ***indicator*** ; alternatively some other physical measurement may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a color change or the formation of turbidity) in the liquid being titrated. The point at which this occurs is called the end point of the titration. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs this represents the ***titration error***. The indicator and experimental conditions should be so selected that the difference between the visible end point and equivalence point is as small as possible.

For use in titrimetric analysis a reaction must have the following conditions:

1- There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent propties.
2- The reaction should be relatively fast. (Most ionic reaction satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of a reaction.
3- There must be an alteration in some physical or chemical property of the solution at the equivalence point.
4- An indicator should be available which, by a change in physical properties (color or formation of a precipitate), should sharply define the end point of the reaction.

Definition of some terms

Titration

Titration is the process in which the standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is complete.

Equivalence point and End point

The equivalence point of a titration is a theoretical point that can not be determined experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of equivalence. This change is called the end point for titration.

Titration error

The difference between the observed end point and the true equivalence point in a titration.

Indicators

Indicators are often added to analyte solution in order to give an observable physical change (end point) at or near the equivalence point. In other wards indicator is a compound having a physical property (usually color) that changes abruptly near the equivalence point of a chemical reaction.

End Points in Volumetric Analysis

Detection of an end point involves the observation of some property of the solution that change in a characteristic way at or near the equivalent point. The properties that have been used for this purpose are numerous and varied; they include:

1. Color due to the reagent, the substance being determined, or an indicator substance.
2. Turbidity changes resulting from the formation or disappearance of solid phase.
3. Electric conductivity of the solution.
4. Electric potential between a pair of electrodes immersed in the solution.
5. Refractive index of the solution.
6. Temperature of the solution.
7. Electric current passing through the solution.

Primary standard

A primary standard is a highly purified compound that serve as a reference material in all volumetric method. The accuracy of method is critically dependent on the properties of this compound. Important requirements for primary standard are:

1- High purity.
2- Stability toward air.
3- Absence of hydrated water.
4- Ready availability at modest cost.
5- Reasonable solubility in titration medium.
6- Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

Compound that meet or even approach these criteria are very few , and only a limited number of primary standard substances are available to the chemist.

Secondary standard

A secondary standard is a compound whose purity has been established by chemical analysis and serves as the reference material for titrmetric method of analysis. Compound such as sodium hydroxide or hydrochloric acid cannot be considered as primary standard since their purity is quite variable. So for instance sodium hydroxide solution must be standardized against potassium hydrogen phethalate (primary standard), which is available in high purity. The standardized sodium hydroxide solution (secondary standard) may be used to standardize solutions.

Standard solution

Standard solution is the reagent of exactly known concentration that is used in titrimetric analysis. Standard solutions play a central role in all titrimetric method of analysis. Therefore we need to consider the desirable properties for such solutions, how they are prepared and how their concentration are expressed.

Desirable properties of standard solutions

The ideal standard solution for titrmetric method will:

1- be sufficiently stable so that it is only necessary to determine the concentration once,

2- react rapidly with the analyte so that the time required between additions of reagent is minimized .
3- react more or less completely with the analyte so that satisfactory end points are realized.
4- Undergo a selective reaction with the analyte that can be described by simple balanced equation.

Few reagents meet all these ideal perfectly.

Methods for establishing the concentration of standard solutions

Two basic methods are used to establish the concentration of such solutions. The first is the direct method in which a carefully weighed quantity of primary standard is dissolved in a suitable solvent and diluted to an exactly known volume in a volumetric flask.

The second is by standardization the process whereby the concentration of a reagent is determined by reaction with a known quantity of a second reagent. A titrant that is standardized against another standard solution is some times referred as a secondary standard solution. If there is a choice, then solution are prepared by the direct method. On the other hand , many reagents lack the properties required for a primary standard and therefore required standardization.

Method for expressing the concentration of standard solution

The concentrations of standard solution are generally expressed in units of either molarity or normality. The first gives the number of moles of reagents contained in 1L of solution, and the second gives the number of equivalents of reagent in the same volume.

Direct titration and back titration

When a titrant reacts directly with an analyte, the procedure is termed a direct titration. It is some times necessary to add an excess of standard titrant and then determine the excess amount by back titration with a second standard titrant. In other wards back titration is a process in which the excess of standard solution used to react with an analyte is determined by titration with a second standard solution. Back – titration are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability. In back – titration, the equivalence point corresponds to the point when the amount of initial titrant is chemically equivalent to the amount af analyte plus the amount of back titrant.

Classification of reaction in titrimetric analysis

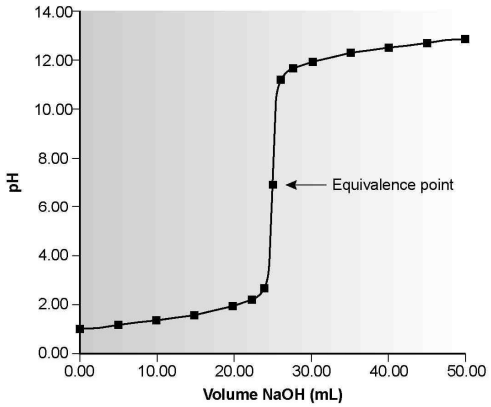
The reaction employed in titrmetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation-reduction reactions, involves a change of oxidation state or, expressed another, 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 (alkalimrtry). The reaction involve 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 af a cyanide with silver nitrate. Ethylendiaminetera-acetic acid, largely as the disodium salt of EDTA, is a very important reagent for complex formation titration and has become on 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.

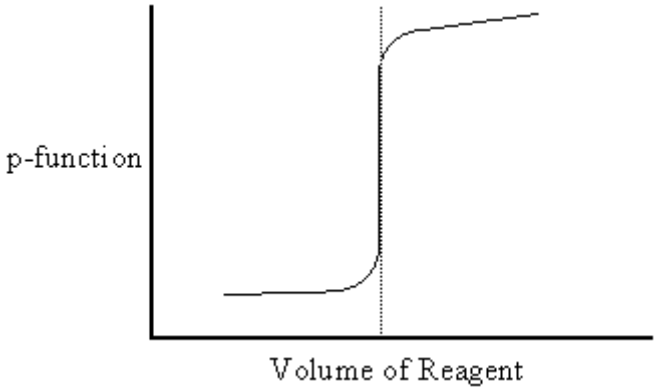
Suppose that the only available indicator changes color at a pH of 6.8. Is this end point close enough to the equivalence point that the titration error may be safely ignored? To answer this question we need to know how the pH changes during the titration.

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.

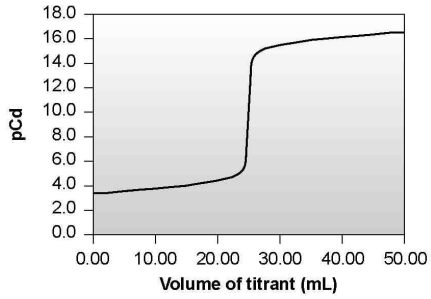
A titration curve is a plot of reagent volume added versus some function of the analyte concentration. Volume of added reagent is generally plotted on the x axis. The measured parameter that is a function of analyte concentration is plotted on the y axis.

Two general titration curve types are seen:

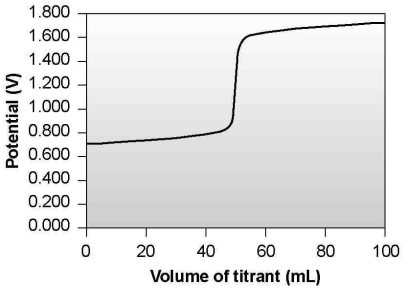
1. Sigmoidal curve - a "z" or "s"-shaped curve where the y axis is a p-function of the analyte (or the reagent reacted with the analyte during titration) or the potential of an ion-specific electrode.



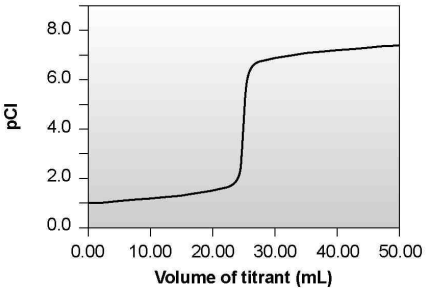
The equivalent point is observed in the middle of the "middle" segment of the "z" or "s."
Examples of Sigmoidal titration curves



Complexation titration

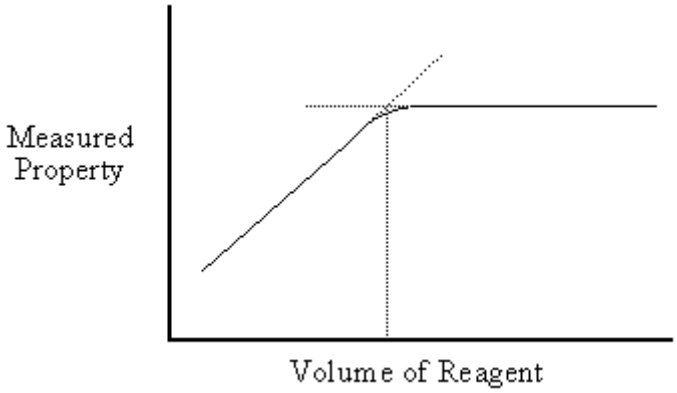


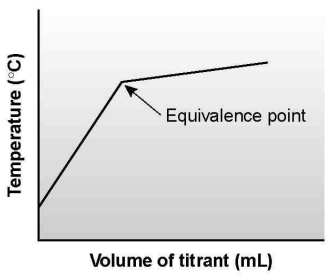
Redox titration



Precipitation titration.

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





Applications of Titrimetry in Pharmaceutical Analysis

Titrimetric methods are still widely used in pharmaceutical analysis because of their robustness, cheapness and capability for high precision. The only requirement of an analytical method that they lack is specificity.

Applications

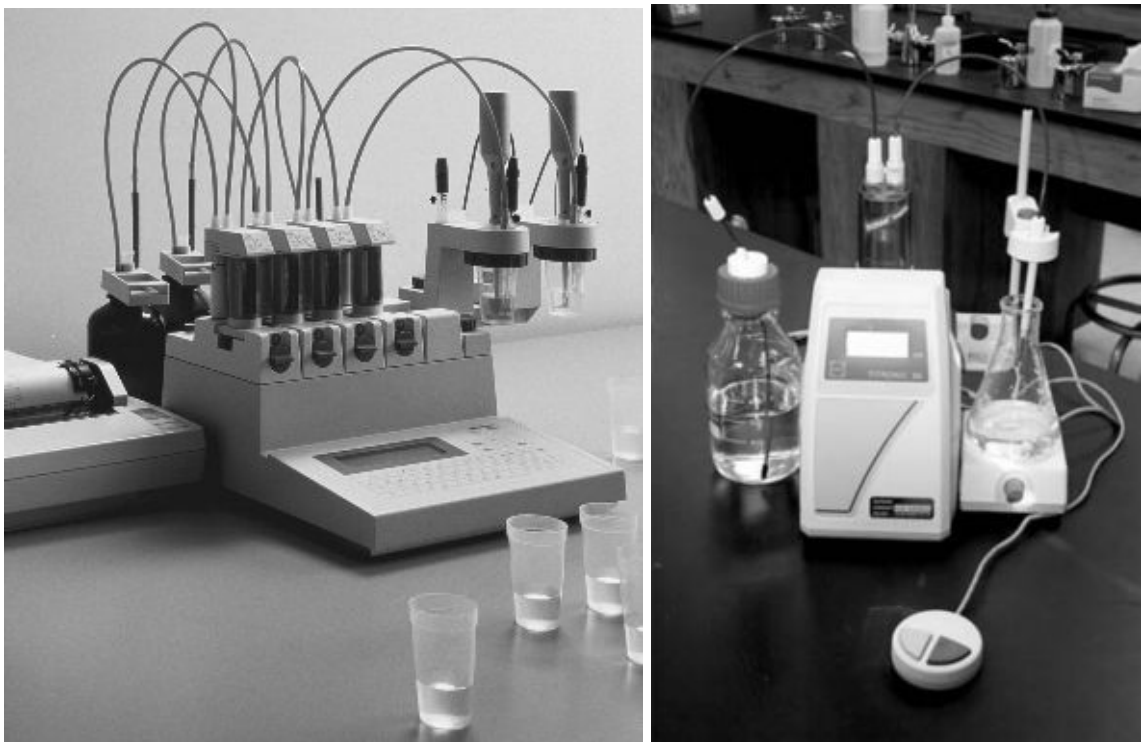
- Provide standard pharmacopoeial methods for the assay of unformulated drugs and excipients and some formulated drugs, e.g. those that lack a strong chromophore.
- Used for standardisations of raw materials and intermediates used in drug synthesis in industry. Suppliers of raw materials may provide these materials at a specified purity which has been assayed titrimetrically to a pharmacopoeial standard.
- Certain specialist titrations, such as the Karl Fischer titration used to estimate water content, are widely used in the pharmaceutical industry.

Advantages

- Capable of a higher degree of precision and accuracy than instrumental methods of analysis.
- The methods are generally robust.
- Analyses can be automated.
- Cheap to perform and do not require specialised apparatus.
- They are absolute methods and are not dependent on the calibration of an instrument.

Limitations

- Non-selective.
- Time-consuming if not automated and require a greater level of operator skill than routine instrumental methods.
- Require large amounts of sample and reagents.
- Reactions of standard solutions with the analyte should be rapid and complete.



Typical instrumentation for performing an automatic titration (automatic titrator).

Titrations Based on Acid-Base Reactions

The earliest acid-base titrations involved the determination of the acidity or alkalinity of solutions, and the purity of carbonates and alkaline earth oxides. Various acid-base titration reactions, including a number of scenarios of base in the burette, acid in the reaction flask, and vice versa, as well as various monoprotic and polyprotic acids titrated with strong bases and various weak monobasic and polybasic bases titrated with strong acids. A **monoprotic acid** is an acid that has only one hydrogen ion (or proton) to donate per fomula. Examples are hydrochloric acid, HCl, a strong acid, and acetic acid, $HC_2H_30_2$, a weak acid. A **polyprotic acid** is an acid that has two or more hydrogen ions to donate per formula. Examples include sulfuric acid, H_2S0_4, a **diprotic acid,** and phosphoric acid, H_3P0_4, a **triprotic** acid.

A **monobasic base** is one that will accept just one hydrogen ion per formula. Examples include sodium hydroxide, NaOH, a strong base; ammonium hydroxide, NH_4OH, a weak base; and sodium bicarbonate, $NaHC0_3$, a weak base. A **polybasic base** is one that will accept two or more hydrogen ions per formula. Examples include sodium carbonate, Na_2CO_3, a **dibasic base,** and sodium phosphate, Na_3P0_4, a **tribasic base.**

Acid-Base Titration Curves

In the overview to the titration we noted that the experimentally determined end point should coincide with the titration's equivalence point. For an acid-base titration, the equivalence point is characterized by a pH level that is a function of the acid-base strengths and concentrations of the analyte and titrant. The pH at the end point, however, may or may not correspond to the pH at the equivalence point. To understand the relationship between end points and equivalence points we must know how the pH changes during a titration. In this section we will learn how to construct titration curves for several important types of acid-base titrations.

Titrating Strong Acids and Strong Bases

For our first titration curve let's consider the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. For the reaction of a strong base with a strong acid the only equilibrium reaction of importance is

$$H_3O^+(aq) + OH^-(aq) = 2H_2O(l)$$

The first task in constructing the titration curve is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know from reaction above that

$$\text{Moles HCl} = \text{moles NaOH}$$

or

$$M_aV_a = M_bV_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is

$$V_{eq} = V_b = \frac{M_aV_a}{M_b} = \frac{(0.100\ \text{M})(50.0\ \text{mL})}{(0.200\ \text{M})} = 25.0\ \text{mL}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH is

$$pH = -\log[H_3O^+] = -\log[HCl] = -\log(0.100) = 1.00$$

The equilibrium constant for reaction is $(K_w)^{-1}$, or 1.00×10^{14}. Since this is such a large value we can treat reaction as though it goes to completion. After adding 10.0 mL of NaOH, therefore, the concentration of excess HCl is

$$[HCl] = \frac{\text{moles excess HCl}}{\text{total volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$= \frac{(0.100\ M)(50.0\ mL) - (0.200\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 0.050\ M$$

giving a pH of 1.30.

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+]^2$$

$$[H_3O^+] = 1.00 \times 10^{-7}\ M$$

Thus, the pH at the equivalence point is 7.00.

Finally, for volumes of NaOH greater than the equivalence point volume, the pH is determined by the concentration of excess OH^-. For example, after adding 30.0 mL of titrant the concentration of OH^- is

$$[OH] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_bV_b - M_aV_a}{V_a + V_b}$$

$$= \frac{(0.200\ M)(30.0\ mL) - (0.100\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 0.0125\ M$$

To find the concentration of H_3O^+, we use the K_w expression

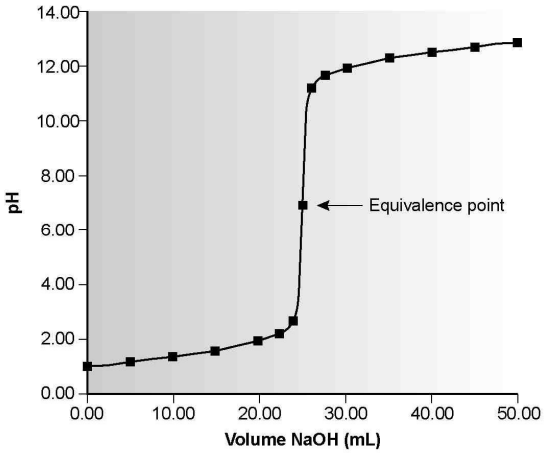
$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}$$

giving a pH of 12.10.

The table and the figure below show additional results for this titration curve.

Data for Titration of 50.00 mL of 0.100 M HCl with 0.0500 M NaOH

Volume (mL) of Titrant	pH
0.00	1.00
5.00	1.14
10.00	1.30
15.00	1.51
20.00	1.85
22.00	2.08
24.00	2.57
25.00	7.00
26.00	11.42
28.00	11.89
30.00	12.50
35.00	12.37
40.00	12.52
45.00	12.62
50.00	12.70



Calculating the titration curve for the titration of a strong base with a strong acid is handled in the same manner, except that the strong base is in excess before the equivalence point and the strong acid is in excess after the equivalence point.

Titrating a Weak Acid with a Strong Base

For this example let's consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH, with 0.100 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\text{Moles } CH_3COOH = \text{Moles NaOH}$$

$$M_a V_a = M_b V_b$$

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 50.0\text{ mL}$$

Before adding any NaOH the pH is that for a solution of 0.100 M acetic acid. Since acetic acid is a weak acid, we calculate the pH using this method

$$CH_3COOH(aq) + H_2O(l) = H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [H_3O^+] = 1.32 \times 10^{-3}$$

We can use the following equation

$$[H_3O^+] = \sqrt{K_a\, c(HA)}$$

At the beginning of the titration the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base.

$$CH_3COOH(aq) + OH^-(aq) = H_2O(l) + CH_3COO^-(aq)$$

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A^-, is a buffer. As we learned before, we can calculate the pH of a buffer using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

The equilibrium constant for the above reaction is large ($K = K_a/K_w = 1.75 \times 10^9$), so we can treat the reaction as one that goes to completion. Before the equivalence point, the concentration of unreacted acetic acid is

$$[CH_3COOH] = \frac{\text{moles unreacted } CH_3COOH}{\text{total volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

and the concentration of acetate is

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_bV_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are

$$[CH_3COOH] = \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 0.0667\text{ M}$$

$$[CH_3COO^-] = \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 0.0167\text{ M}$$

giving a pH of

$$pH = 4.76 + \log \frac{[0.0167]}{[0.0667]} = 4.16$$

A similar calculation shows that the pH after adding 20.0 mL of NaOH is 4.58.

At the equivalence point, the moles of acetic acid initially present and the moles of NaOH added are identical. Since their reaction effectively proceeds to completion, the predominate ion in solution is CH_3COO^-, which is a weak base. To calculate the pH we first determine the concentration of CH_3COO^-.

$$[CH_3COO^-] = \frac{\text{moles } CH_3COOH}{\text{total volume}} = \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 50.0\text{ mL}} = 0.0500\text{ M}$$

The pH is then calculated for a weak base.

$$CH_3COO^-(aq) + H_2O(l) = OH^-(aq) + CH_3COOH(aq)$$

$$[OH^-] = \sqrt{K_b\, c(B)}$$

$$[OH^-] = 5.34 \text{ X } I0^{-6}\text{ M}$$

The concentration of H_3O^+, therefore, is 1.87×10^{-9}, or a pH of 8.73.

After the equivalence point NaOH is present in excess, and the pH is determined in the same manner as in the titration of a strong acid with a strong base. For example, after adding 60.0 mL of NaOH, the concentration of OH^- is

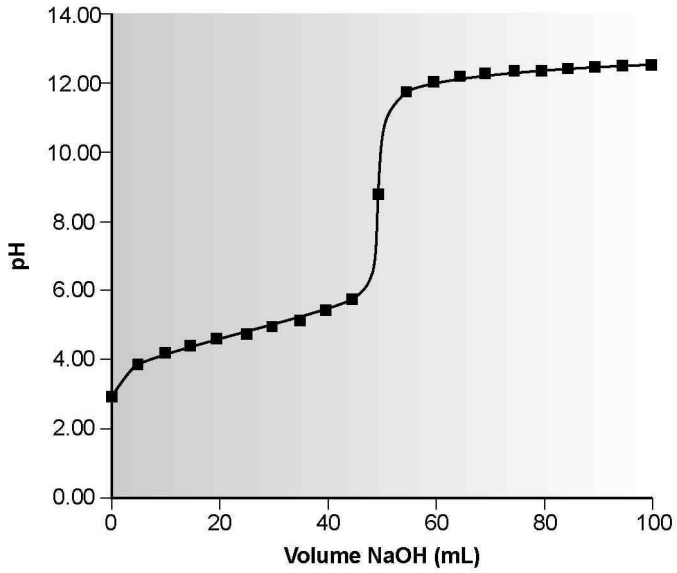
$$[OH] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_bV_b - M_aV_a}{V_a + V_b} = 0.00909\text{M}$$

$$= \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 0.0125\text{ M}$$

giving a pH of 11.96. The table and figure below show additional results for this titration.

The calculations for the titration of a weak base with a strong acid are handled in a similar manner except that the initial pH is determined by the weak base, the pH at the equivalence point by its conjugate weak acid, and the pH after the equivalence point by the concentration of excess strong acid.

Volume of NaOH (mL)	pH
0.00	2.88
5.00	3.81
10.00	4.16
15.00	4.39
20.00	4.58
25.00	4.76
30.00	4.94
35.00	5.13
40.00	5.36
45.00	5.71
48.00	6.14
50.00	8.73
52.00	11.29
55.00	11.68
60.00	11.96
65.00	12.12
70.00	12.22
75.00	12.30
80.00	12.36
85.00	12.41
90.00	12.46
95.00	12.49
100.00	12.52



Data and titration curve for Titration of 50.0 mL of 0.100 M Acetic Acid with 0.100 M NaOH

Method for finding the end point in acid-base titration

1- Finding the End Point with a Visual Indicator.

2- Finding the End Point by Monitoring pH.

3- Finding the End Point by Monitoring Temperature.

Precipitation Titrations

Thus far we have examined titrimetric methods based on acid-base reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can form the basis for a titration. We call this type of titration a **precipitation titration.**

One of the earliest precipitation titrations, developed at the end of the eighteenth century, was for the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(N0_3)_2$, was used as a titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$ The end point was signaled by noting when the addition of titrant ceased to generate additional precipitate. The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag^+ and halide ions.

Precipitation Reactions

A precipitation reaction occurs when two or more soluble species combine to form an insoluble product that we call a **precipitate.** The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. When a solution of lead nitrate is added to a solution of potassium chloride, for example, a precipitate of lead chloride forms. We usually write the balanced reaction as a net ionic equation, in which only the precipitate and those ions involved in the reaction are included. Thus, the precipitation of $PbCl_2$ is written as

$$Pb^{2+}(aq) + 2Cl^{-}(aq) = PbCl_2(s)$$

In the equilibrium treatment of precipitation, however, the reverse reaction describing the dissolution of the precipitate is more frequently encountered.

$$PbCl_2(s) = Pb^{2+}(aq) + 2Cl^{-}(aq)$$

The equilibrium constant for this reaction is called the **solubility product,** K_{sp}, and is given as

$$K_{sp} = [Pb^{2+}]\,[Cl\text{-}]^2 = 1.7 \text{ X } l0^{-5}$$

Note that the precipitate, which is a solid, does not appear in the K_{sp} expression. It is important to remember, however, that equation is valid only if $PbCl_2(s)$ is present and in equilibrium with the dissolved Pb^{2+} and Cl.

Titration Curves

The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant. For example, in an analysis for I using Ag^+ as a titrant

$$Ag^{+}(aq) + I\ (aq) = AgI(s)$$

the titration curve may be a plot of pAg or pI as a function of the titrant's volume. As we have done with previous titrations, we first show how to calculate the titration curve.

Calculating the Titration Curve

As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+. The reaction in this case is

$$Ag^{+}(aq) + Cl^{-}\ (aq) = AgCl(s)$$

The equilibrium constant for the reaction is

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^{9}$$

Since the equilibrium constant is large, we may assume that Ag^+ and Cl^- react completely.

By now you are familiar with our approach to calculating titration curves. The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{Moles } Ag^+ = \text{moles } Cl^-$$

or

$$M_{Ag}V_{Ag} = M_{Cl}V_{Cl}$$

Solving for the volume of Ag^+

$$V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.050\ M)(50.0\ mL)}{(0.100\ M)} = 25.0\ mL$$

shows that we need 25.0 mL of Ag^+ to reach the equivalence point.

Before the equivalence point Cl^- is in excess. The concentration of unreacted Cl^- after adding 10.0 mL of Ag^+, for example, is

$$[Cl^-] = \frac{\text{moles excess } Cl^-}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.050\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 2.50 \times 10^{-2}\ M$$

If the titration curve follows the change in concentration for Ch, then we calculate pCl as

$$pCl = -\log[Cl^-] = -\log(2.50 \times 10^{-2}) = 1.60$$

However, if we wish to follow the change in concentration for Ag^+ then we must first calculate its concentration. To do so we use the K_{sp} expression for AgCl

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Solving for the concentration of Ag^+

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9}\ M$$

gives apAg of 8.14.

At the equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. Using the solubility product expression

$$K_{sp}=[Ag^+][Cl^-] =[Ag^+]^2 = 1.8 \times 10^{-10}$$

gives

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5} M$$

At the equivalence point, therefore, pAg and pCl are both 4.89.

After the equivalence point, the titration mixture contains excess Ag^+. The concentration of Ag^+ after adding 35.0 mL of titrant is

$$[Ag^+] = \frac{\text{moles excess } Ag^+}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.10\ M)(35.0\ mL) - (0.050\ M)(50.0\ mL)}{50.0\ mL + 35.0\ mL} = 1.18 \times 10^{-2}\ M$$

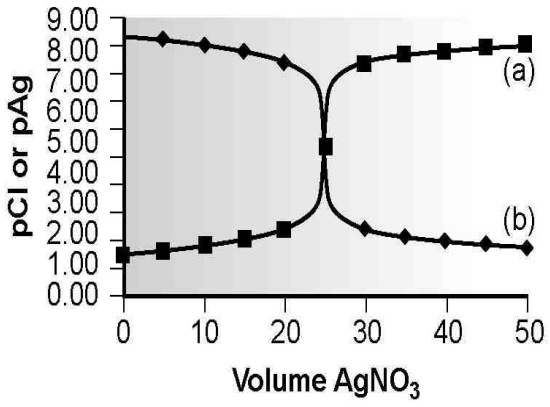
or a pAg of 1.93. The concentration of Cl is

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{1.18 \times 10^{-2}} = 1.5 \times 10^{-8}\ M$$

or a pCl of 7.82.

Volume $AgNO_3$ (mL)	pCl	pAg
0.00	1.30	—
5.00	1.44	8.31
10.00	1.60	8.14
15.00	1.81	7.93
20.00	2.15	7.60
25.00	4.89	4.89
30.00	7.54	2.20
35.00	7.82	1.93
40.00	7.97	1.78
45.00	8.07	1.68
50.00	8.14	1.60

Data for Titration of 50.0 mL of 0.0500 M Cl" with 0.100 M Ag^+



Precipitation titration curve for 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+. (a) pCl versus volume of titrant; (b) pAg versus volume of titrant

Methods for finding the end point in Precipitation Titration

1- Finding the End Point with a Visual Indicator

There three methods to find end point in precipitation titration with visual indicator. First important visual indicator to be developed was the ***Mohr method*** for Cl^- using Ag^+ as a titrant. By adding a small amount of K_2CrO_4 to the solution containing the analyte, the formation of a precipitate of reddish-brown Ag_2CrO_4 signals the end point.

$$Ag^+ + Cl^- = AgCl_{(s)} \quad \text{White precipitate}$$

$$2Ag^+ + CrO_4^{2-} = Ag_2CrO_{4(s)} \quad \text{Red precipitate}$$

A second end point is the ***Volhard method*** in which Ag^+ is titrated with SCN^- in the presence of Fe^{3+}. The end point for the titration reaction

$$Ag^+_{(aq)} + SCN^-_{(aq)} = AgSCN_{(s)}$$

is the formation of the reddish colored $Fe(SCN)^{2+}$ complex.

$$SCN^-_{(aq)} + Fe^{3+}_{(aq)} = Fe(SCN)^{2+}_{(aq)}$$

The titration must be carried out in a strongly acidic solution to achieve the desired end point.

A third end point is evaluated with ***Fajans' method***, which uses an adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution. For example, when titrating Cl^- with Ag^+ the anionic dye dichloro-fluoroscein is used as the indicator. Before the end point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess Cl^-. The anionic indicator is repelled by the precipitate and remains in solution where it has a greenish yellow color. After the end point, the precipitate has a positive surface charge due to the adsorption of excess Ag^+. The anionic indicator now adsorbs to the precipitate's surface where its color is pink. This change in color signals the end point.

2- Finding the End Point Potentiometrically.

Complexation Reactions and Titrations

Introduction

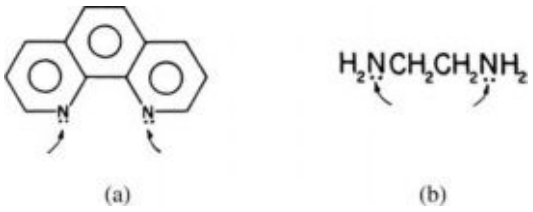
Complexation ractions are important in many areas of science. Complexes play an important role in many chemical and biochemical process. For example the heme molecule in blood holds the iron atom tightly because the nitrogen of the heme form strong complexing bonds, that is nitrogen is a good complexer. Complextion reactions are widely used in analytical chemistry. One of the first uses of these reactions was for titrating cations.

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ***ligand*** must have at least one pair of unshared electrons available for bond formation.

A ligand is an ion or molecule that forms a covalent bond with a cation or neutral metal atom by donating a pair of electrons, which are then shared by the two. Ligands can be classified into inorganic ligands such as water, ammonia, and halide ions, and organic ligands such as 8-hydroxyquinoline.

The widely compounds (ligands) used in complexemetric titrations called ***chelates***. A chelate is produced when a metal ion coordinates with two or more doner groups of a single ligand to form a five or six member heterocyclic ring.

A ligand that has:
single donor group is called ***unidentate***
two donor groups is called ***bidentate***
three donor groups is called ***tridentate***
four donor groups is called ***tetradentate***
five donor groups is called ***pentadentate***
six donor groups is called ***hexadentate***



Two bidentate ligands: (a) 1,10 phenanthroline, and (b) ethylenediamine. The arrows point out the bonding sites.

Tetradentate and hexadentate ligands are more satisfactory as titrants than ligands with a lesser n umber of donor groups because their reactions with cations are more complete and because they tend to form 1:1 complexes.

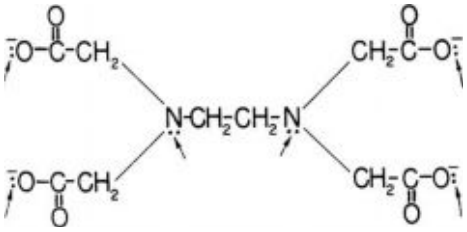
Aminocarboxylic acid titration

Aminocarboxylic acid compounds are multidentate ligands capable of forming stable 1:1 complexes with metal ions. The most widely used of the new ligands was ethylendiaminetetraacetic acid EDTA which is a hexadentate ligand and the most important and widely used reagent in titrimetry. The advantages of EDTA is

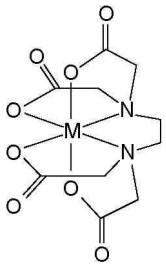
1- form strong 1:1 complexes.
2- react with many metal ions.

Chemistry and Properties of EDTA

The structure of EDTA is shown in below. EDTA, which is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons.



The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal-EDTA complexes have a 1:1 stoichiometry.



six-coordinate metal-EDTA complex.

Metal—EDTA Formation Constants

To illustrate the formation of a metal-EDTA complex consider the reaction between Cd^{2+} and EDTA

$$Cd^{2+}(aq) + Y^{4-}(aq) = CdY^{2-}(aq)$$

where Y^{4-} is a shorthand notation for the chemical form of EDTA. The formation constant for this reaction

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,[Y^{4-}]} = 2.9 \times 10^{16}$$

is quite large, suggesting that the reaction's equilibrium position lies far to the right.

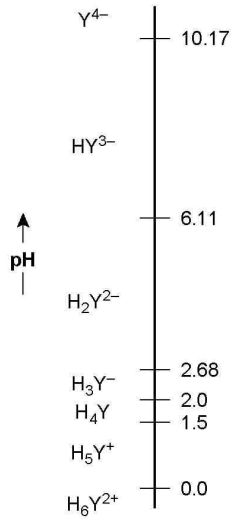
EDTA Is a Weak Acid

Besides its properties as a ligand, EDTA is also a weak acid. The fully protonated form of EDTA, H_6Y^{2+}, is a hexaprotic weak acid with successive pK_a values of

$pK_{al} = 0.0$ $pK_{a2} = 1.5$ $pK_{a3} = 2.0$ $pK_{a4} = 2.68$ $pK_{a5} = 6.11$ $pK_{a6} = 10.17$

The first four values are for the carboxyl protons, and the remaining two values are for the ammonium protons.

A ladder diagram for EDTA is shown below.



The species Y^{4-} becomes the predominate form of EDTA at pH levels greater than 10.17. It is only for pH levels greater than 12 that Y^{4-} becomes the only significant form of EDTA.

Conditional Metal—Ligand Formation Constants

Recognizing EDTA's acid-base properties is important. The formation constant for CdY^{2-} assumes that EDTA is present as Y^{4-}. If we restrict the pH to levels greater than 12, then equation

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,[Y^{4-}]} = 2.9 \times 10^{16}$$

provides an adequate description of the formation of CdY^{2-}. For pH levels less than 12, however, K_f overestimates the stability of the CdY^{2-} complex. At any pH a mass balance requires that the total concentration of unbound EDTA equal the combined concentrations of each of its forms.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

To correct the formation constant for EDTA's acid-base properties, we must account for the fraction, $\alpha_{Y^{4-}}$, of EDTA present as Y^{4-}.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

Values of $\alpha_{Y^{4-}}$ for Selected pHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

Solving equation

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,[Y^{4-}]} = 2.9 \times 10^{16}$$

for $[Y^{4-}]$ and substituting gives

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,\alpha_{Y^{4-}}\,C_{EDTA}}$$

If we fix the pH using a buffer, then $\alpha_{Y^{4-}}$ is a constant. Combining $\alpha_{Y^{4-}}$ with K_f gives

$$K_f' = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,C_{EDTA}}$$

where K_f' is a **conditional formation constant** whose value depends on the pH. As shown in following table for CdY^{2-},

pH	K_f'	pH	K_f'
2	1.1×10^{3}	8	1.6×10^{14}
3	7.3×10^{5}	9	1.5×10^{15}
4	1.0×10^{8}	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}

the conditional formation constant becomes smaller, and the complex becomes less stable at lower pH levels.

EDTA Must Compete with Other Ligands

To maintain a constant pH, we must add a buffering agent. If one of the buffer's components forms a metal-ligand complex with Cd^{2+}, then EDTA must compete with the ligand for Cd^{2+}. For example, an NH_4^+/NH_3 buffer includes the ligand NH_3, which forms

several stable Cd^{2+}-NH_3 complexes. EDTA forms a stronger complex with Cd^{2+} and will displace NH_3. The presence of NH_3, however, decreases the stability of the Cd^{2+}-EDTA complex.

We can account for the effect of an **auxiliary complexing agent,** such as NH_3, in the same way we accounted for the effect of pH. Before adding EDTA, a mass balance on Cd^{2+} requires that the total concentration of Cd^{2+}, C_{cd}, be

$$C_{cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2{}^{2+}] + [Cd(NH_3)_3{}^{2+}] + [Cd(NH_3)_4{}^{2+}]$$

The fraction, $\alpha_{cd}{}^{2+}$ present as uncomplexed Cd^{2+} is

$$\alpha_{cd}{}^{2+} = \frac{[Cd^{2+}]}{C_{cd}}$$

Solving equation

$$K_f{}' = \alpha_Y{}^{4-} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\, C_{EDTA}}$$

for $[Cd^{2+}]$ and substituting gives

$$K_f{}' = \alpha_Y{}^{4-} \times K_f = \frac{[CdY^{2-}]}{\alpha_{cd}{}^{2+}\, C_{cd}\, C_{EDTA}}$$

If the concentration of NH_3 is held constant, as it usually is when using a buffer, then we can rewrite this equation as

$$K_f{}'' = \alpha_{cd}{}^{2+} \times \alpha_Y{}^{4-} \times K_f = \frac{[CdY^{2-}]}{C_{cd}\, C_{EDTA}}$$

where $K_f{}''$ is a new conditional formation constant accounting for both pH and the presence of an auxiliary complexing agent. Values of $\alpha_M{}^{n+}$ for several metal ions are provided in following table

$[NH_3]$ (M)	α_{Ag^+}	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$	$\alpha_{Zn^{2+}}$
1	1.00×10^{-7}	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}	3.95×10^{-10}
0.5	4.00×10^{-7}	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}	6.27×10^{-9}
0.1	9.98×10^{-6}	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}	3.68×10^{-6}
0.05	3.99×10^{-5}	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}	5.45×10^{-5}
0.01	9.83×10^{-4}	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}	1.82×10^{-2}
0.005	3.86×10^{-3}	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}	1.27×10^{-1}
0.001	7.95×10^{-2}	9.99×10^{-1}	6.90×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}	7.48×10^{-1}

Complexometric EDTA Titration Curves

Now that we know something about EDTA's chemical properties, we are ready to evaluate its utility as a titrant for the analysis of metal ions. To do so we need to know the shape of a complexometric EDTA titration curve. We saw that an acid-base titration curve shows the change in pH following the addition of titrant. The analogous result for a titration with EDTA shows the change in pM, where M is the metal ion, as a function of the volume of EDTA.

Calculating the Titration Curve

As an example, let's calculate the titration curve for 50.0 mL of 5.00 X 10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3. The formation constant for Cd^{2+}-EDTA is 2.9 X 10^{16}.

Since the titration is carried out at a pH of 10, some of the EDTA is present in forms other than Y^{4-}. In addition, the presence of NH_3 means that the EDTA must compete for the Cd^{2+}. To evaluate the titration curve, therefore, we must use the appropriate conditional formation constant. We find that α_Y^{4-} is 0.35 at a pH of 10, and that α_{cd}^{2+} is 0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, we calculate that the conditional formation constant is

$$K_f'' = \alpha_{cd}^{2+} \times \alpha_Y^{4-} \times K_f = (0.35)(0.0881)(2.9 \times 10^{16}) = 8.9 \times 10^{14}$$

Because K_f'' is so large, we treat the titration reaction as though it proceeds to completion.

The first task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that

$$\text{Moles EDTA} = \text{Moles } Cd^{2+}$$

or

$$M_{EDTA}V_{EDTA} = M_{Cd}V_{Cd}$$

Solving for the volume of EDTA

$$V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(0.005\ \text{M})(50.0\ \text{mL})}{(0.01\ \text{M})} = 25.0\ \text{mL}$$

shows us that 25.0 mL of EDTA is needed to reach the equivalence point.

Before the equivalence point, Cd^{2+} is in excess, and pCd is determined by the concentration of free Cd^{2+} remaining in solution. Not all the untitrated Cd^{2+} is free (some is complexed with NH_3), so we will have to account for the presence of NH_3.

For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

$$C_{Cd} = \frac{\text{moles excess } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL) - (0.010\ M)(5.0\ mL)}{50.0\ mL + 5.0\ mL} = 3.64 \times 10^{-3}\ M$$

To calculate the concentration of free Cd2+ we use equation

$$\alpha_{cd^{2+}} = \frac{[Cd^{2+}]}{C_{cd}}$$

$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(3.64 \times 10^{-3}\ M) = 3.21 \times 10^{-4}\ M$

Thus, pCd is

$pCd = -\log[Cd^{2+}] = -\log(3.21 \times 10^{-4}) = 3.49$

At the equivalence point, all the Cd^{2+} initially present is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. To find pCd we must first calculate the concentration of the complex.

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL)}{50.0\ mL + 25.0\ mL} = 3.33 \times 10^{-3}\ M$$

Letting the variable x represent the concentration of Cd^{2+} due to the dissociation of the CdY^{2-} complex, we have

$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\,C_{EDTA}} = \frac{3.33 \times 10^{-3}}{(x)\,(x)} = 8.94 \times 10^{14}$$

$X = C_{Cd} = 1.93 \times 10^{-9}\ M$

Once again, to find the [Cd2+] we must account for the presence of NH_3; thus
$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(1.93 \times 10^{-9}\ M) = 1.70 \times 10^{-10}\ M$
giving pCd as 9.77.

After the equivalence point, EDTA is in excess, and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. Examining the equation for the complex's conditional formation constant, we see that to calculate C_{Cd} we must first calculate $[CdY^{2-}]$ and C_{EDTA}. After adding 30.0 mL of EDTA, these concentrations are

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 3.13 \times 10^{-3}\ M$$

$$C_{EDTA} = \frac{\text{moles excess EDTA}}{\text{total volume}} = \frac{M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.01\ M)(30.0\ mL) - (0.005\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 6.25 \times 10^{-4}\ M$$

Substituting these concentrations into equation

$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\,C_{EDTA}}$$

and solving for C_{Cd} gives

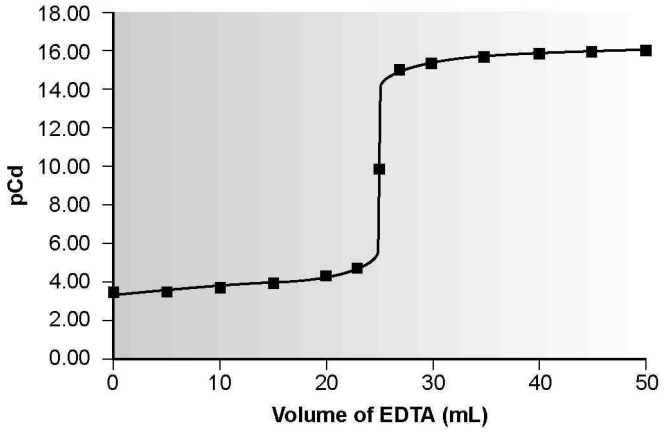
$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\,C_{EDTA}} = \frac{3.13 \times 10^{-3}\ M}{C_{cd}\,(6.25 \times 10^{-4}\ M)} = 8.94 \times 10^{14}$$

$$C_{Cd} = 5.6 \times 10^{-15}\ M$$

Thus,

$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(5.6 \times 10^{-15}\ M) = 4.93 \times 10^{-16}\ M$

and pCd is 15.31.



Complexometric titration curve for 50.0 mL of 5.00 x 10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 in the presence of 0.0100 M NH_3.

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01

Data for Titration of 5.00 x 10^{3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M NH_3

Methods for finding the end point in Precipitation Titration

1- Finding the End Point with a Visual Indicator.

Most indicators for complexation titrations are organic dyes that form stable complexes with metal ions. These dyes are known as **metallochromic indicators.**

2- Finding the End Point by Monitoring Absorbance.