LECTURE- 8

Volumetric Methods of Analysis
Titrimetric Analysis

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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The term volumetric analysis was used for this form of quantitative determination but it has now been replaced by titrimetric analysis.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 properties.

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.

$$TE = V_{ep} - V_{eq}$$

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 (alkalimertry). 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.*

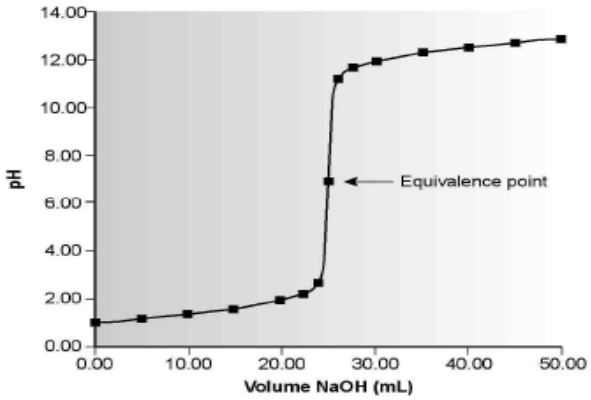
2- Precipitation reaction. These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with solution of chloride. No change in oxidation state occurs.

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.



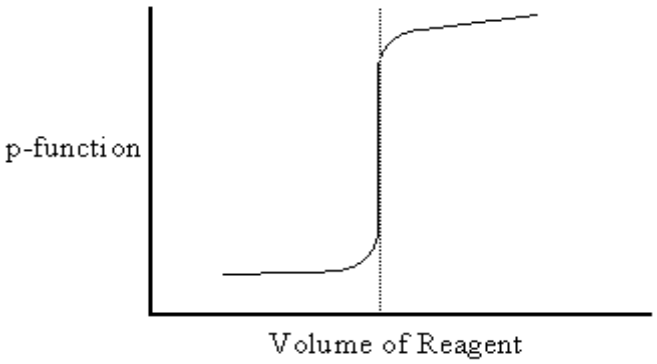
Acid-base titration curve for 25.0 mL of 0.100 M HCl with 0.100 M NaOH.

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.

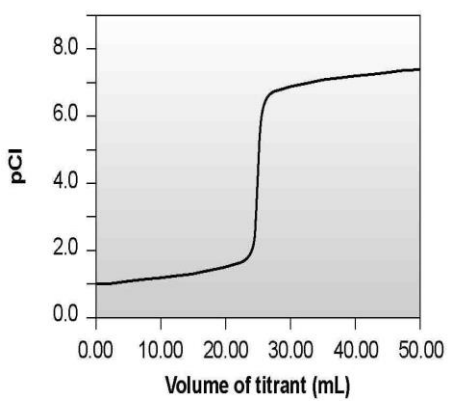
A ***titration curve*** provides us with a visual picture of how a property, such as pH, changes as we add titrant. We can measure this titration curve experimentally by suspending a pH electrode in the solution containing the analyte, monitoring the pH as titrant is added. We can also calculate the 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.

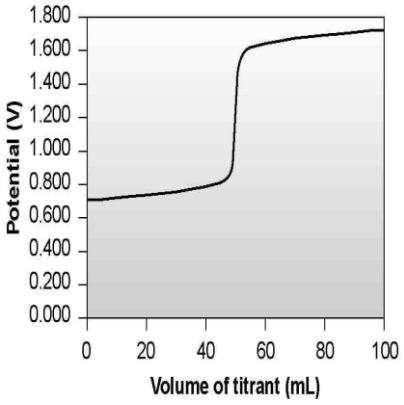
Two general titration curve types are seen:
1. Sigmoidal curve - a "z" or "s"-shaped curve where the y axis is a p-function of the analyte (or the reagent reacted with the analyte during titration) or the potential of an ion-specific electrode.



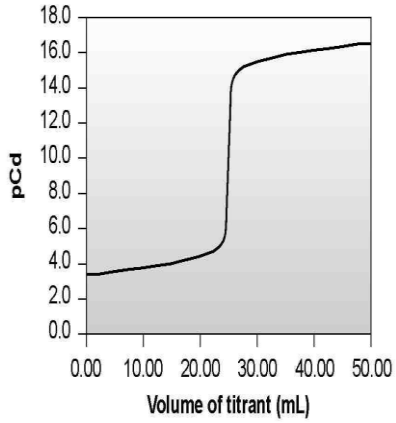
The equivalent point is observed in the middle of the "middle" segment of the "z" or "s."
Examples of Sigmoidal titration curves



Precipitation titration.

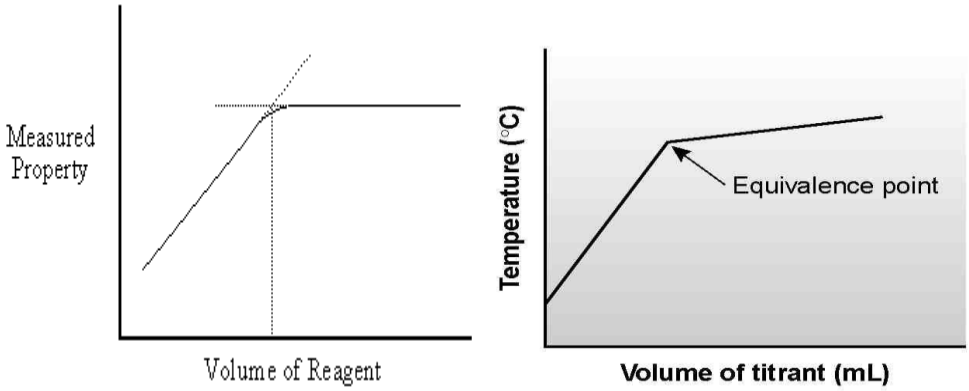


Redox titration



Complexation titration

2. Linear-segment curve - a curve generally consisting of two line segments that intersec 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).