

Additional Lecture:
TITRATION
BASICS

Definition and Applications

Titration is the incremental addition of a reagent solution (called *titrant*) to the analyte until the reaction is complete

Common applications:

1. Determine purity of analyte – Ex. Soda ash purity lab
2. Determine concentration of analyte – Ex. Standardization lab

Example of industries that use titrations

Food and beverage – Ex. Salt content of food; Acid content of wine

Detergent manufacturing – Ex. Anionic surfactant content of detergents

Metallurgy – Ex. Cu, Cr and Ni contents of electroplating baths

Environmental firms – Ex. Total hardness of water (due to Mg^{2+} and Ca^{2+})

Major requirements for a titration reaction:

- Large K_{eq} \Rightarrow reaction goes to completion
- Fast \Rightarrow speed; productivity

Types of Reactions Used in Titration

Acid-base – Ex. Standardization of HCl with Na_2CO_3

Complexometric – Ex. Determining Ca^{2+} in water by EDTA titration

Redox – Ex. Cu, Cr and Ni contents of electroplating baths

Precipitation – Ex. Salt content in crisps, ketchup and food

The Standard Solution

A **standard solution** is a reagent solution of known concentration used in titration

- Usually the *titrant* – Ex. You used your standard 0.1 M HCl to determine purity of soda ash
- Typically prepared from a *primary standard* – Ex. You used primary standard sodium carbonate to standardize $\text{HCl}_{(\text{aq})}$ (also primary standard KHP to standardize $\text{NaOH}_{(\text{aq})}$)

A **primary standard** is a highly pure (at least 99.99 %) compound that serves as *reference material* in all volumetric methods

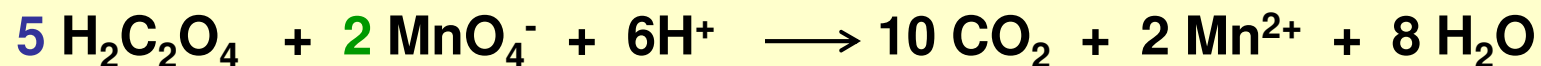
Equivalence Point vs. End Point

Q. How do we know when a titration reaction is complete?

- When we perform a titration, we use an **indicator** that changes color at or near completion of reaction.
 - ❖ Color change is referred to as the **end point** of a titration
 - ❖ Technically, the *equivalence point* of the titration is the point at which exactly enough titrant has been added to react with all of the analyte.
 - ❖ Thus, at the **equivalence point**, the ***number of moles of titrant*** added corresponds exactly to the ***number of moles of substance*** being titrated according to the reaction stoichiometry

Equivalence Point

Example: Redox reaction involving permanganate



Oxalic acid
Analyte

Permanganate
Titrant

❖ At the *equiv. pt.*:

5 mol H₂C₂O₄ have reacted with **2 mol MnO₄⁻**

NOTE: It is difficult to determine exactly when the equivalence point is reached based on # moles.

❖ Reason for use of indicator and stopping the titration when the end point (color change) is reached

Titration Error

Titration error = the difference between the end point and the equivalence point



Flask **before** endpoint...



... ..approximately **at endpoint...**
(very faint pink tinge)

➤ Small titration error



...**after** endpoint (overshot)

➤ Big titration error

Equivalence Point Detection Methods

(1) **Indicator method** = based on color change of indicator

A dye whose color change depends on pH

- Most commonly used

(2) **Potentiometric method** = based on sudden change in voltage or current between a pair of electrodes

- Ex. Alkalinity lab (pH change depends on voltage change)

(3) **Absorbance method** = based on absorbance of light

- Ex. Product absorbs light => absorption increases as product forms

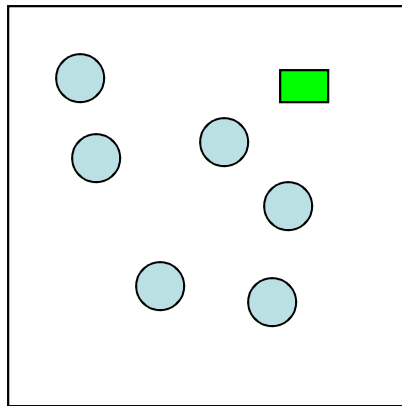
- Equivalence point is reached when absorbance starts to level off –

Why?

Product no longer forms when reaction is complete

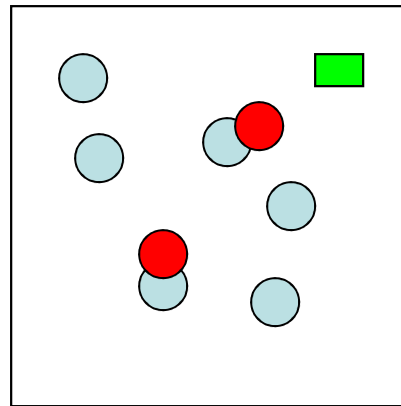
Indicator Method: Titration of Cl^- with Ag^+

Before titration



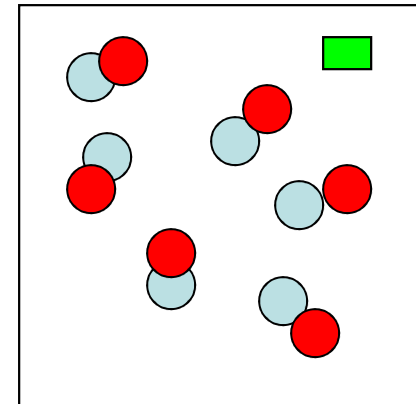
Only a fixed amount of Cl^- in solution plus “free” indicator

During titration
(before the equivalence point)

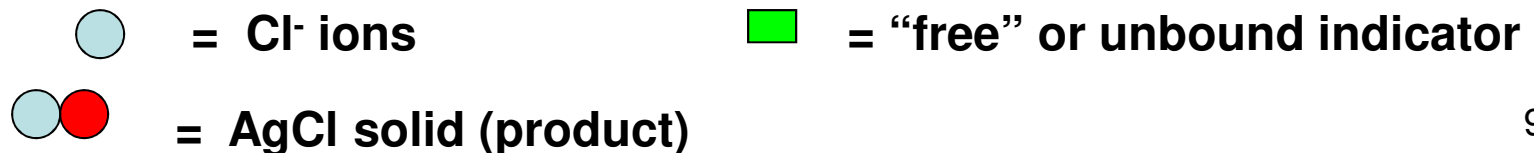


Added titrant reacts with Cl^- to form product, solid AgCl

At the equivalence point of titration

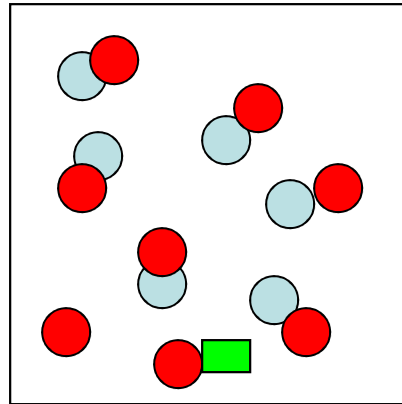


All the analyte Cl^- has reacted with an equivalent amount of titrant

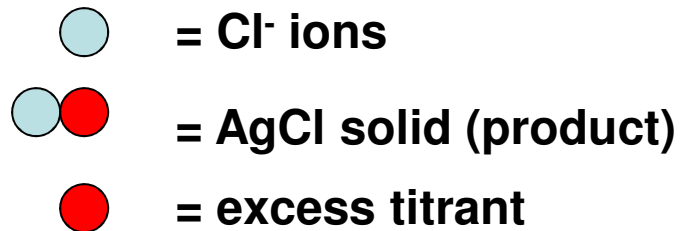


Indicator Methods

After the
equivalence point



Small amount of excess titrant reacts with
indicator, causing color change



Types of Chemical Reactions Used in Titration

(1) Acid/Base reactions:

Examples: Acid content in wine, milk. Acid content in ketchup. Content of inorganic acids like sulfuric acid.

(2) Precipitation reactions:

Examples: Salt content in crisps, ketchup and food; Silver content in coins, Sulfate content in mineral water; Sulfate content in electroplating bath

(3) Redox reactions:

Examples: Content of copper, chromium and nickel in electroplating baths

(4) Complexometric reactions:

Examples: Total hardness of water (Mg and Ca); Calcium content in milk and cheese; Cement analysis

(5) Colloidal precipitation reaction:

Examples: Anionic surfactant content in detergents; Anionic surfactant content in washing powders; Anionic surfactant content in liquid cleanser.

Source: Mettler-Toledo Homepage

http://us.mt.com/mt/faq/FAQ_entry_level_titration_Editorial-Faq_11175423902211.jsp

Advantages of titration

- ❖ Classical, well-known analytical technique
- ❖ Fast
- ❖ Very accurate and precise technique
- ❖ High degree of automation
- ❖ Good price/performance ratio compared to more sophisticated techniques
- ❖ It can be used by low-skilled and trained operators
- ❖ No need for highly specialized chemical knowledge

Source: Mettler-Toledo Homepage

http://us.mt.com/mt/faq/FAQ_entry_level_titration_Editorial-Faq_11175423902231.jsp

Problem Solving: Titrations

Sample problem: How many mL of 0.100 M KI are needed to react with 40.0 mL of 0.0400 M $\text{Hg}_2(\text{NO}_3)_2$.

Back Titrations

Back titration is a technique which allows the user to find the concentration of an analyte by reacting it with an **excess volume of another reactant** of known concentration. The resulting mixture is then titrated back, taking into account the molarity of the excess which was added.

Uses of Back Titration:

- ❖ When the sample is not soluble in water
- ❖ When the sample contains impurities that interfere with forward titration, or
- ❖ When the end-point is more easily identified than in forward titration.

http://en.wikipedia.org/wiki/Back_titration

Problem Solving: Titrations

Sample problem 2: Limestone consists mainly of the mineral calcite, CaCO_3 . The carbonate content of 0.5413 g powdered limestone was measured by suspending the powder in water, adding 10.00 mL of 1.396 M HCl and heating to dissolve the solid and expel CO_2 :



Calcium carbonate
(MM 100.087)

The excess acid required 39.96 mL of 0.1004 M NaOH for complete titration to a phenolphthalein end point. Find the mass % of calcite in the limestone.

Problem Solving: Titrations
