Introduction to Titrimetry

The first text on titrations was written by K.W. Schwarz in 1853 - he said in his foreword:

> *"With the aid of titrimetric analysis, analytical chemistry could be introduced into practical life. I would be contented if even to a small extent I could open the door through which science could enter into the life of industry and technology"*

opus® titration
Motorised titration ensures reproducible results

Today titrations are still important

- They provide up to a part per thousand (ppth) precision
- Relatively easy to perform
- Only a small portion of the possible chemical reactions meet the stringent requirements

What Are Titrations?

- Addition of a solution of known concentration (titrant) to a solution of unknown concentration (analyte).
- Titrations are based on stoichiometric reactions

$$aA + bB = cC$$

- We react the analyte (A) with a reagent known as the titrant (B).

- When we have added exactly the stoichiometric amount of titrant we have reached the **equivalence point**.

$$mol(A)/a = mol(B)/b$$

Example: 2A + B = C; and there are 10 moles of A, how many moles B do we need?

- The amount of titrant needed to reach the equivalence point can be used to calculate the amount of analyte originally present.

- We must know the stoichiometry of the titration reaction
- We must know the concentration and volume of titrant used (thus the number of moles of titrant used)

Requirements of a Titration Reaction

- Rxn must be quantitatively complete
  - This means ≥ 99.9 % complete (so that less than 0.1 % (or 1 ppth) remains unreacted)
  - Can be predicted from equilibrium constants
- Rxn must be rapid
  - Titration needs to be performed in a reasonable time period
- The stoichiometry must be well defined, and known
- A method must be available to determine the equivalence point

Types of Titration Reactions

1) Precipitation

$A_{(aq)} + B_{(aq)} = AB_{(s)}$

2) Acid-Base reaction

$H^+ + OH^- = H_2O$ (strong acids or bases)

$HA + OH^- = H_2O + A^-$ (weak acids)

$A^- + H^+ = H_2O + HA$ (weak bases)

3) Complexation reaction

$Zn^{2+} + 4NH_3 = Zn(NH_3)_4^{2+}$

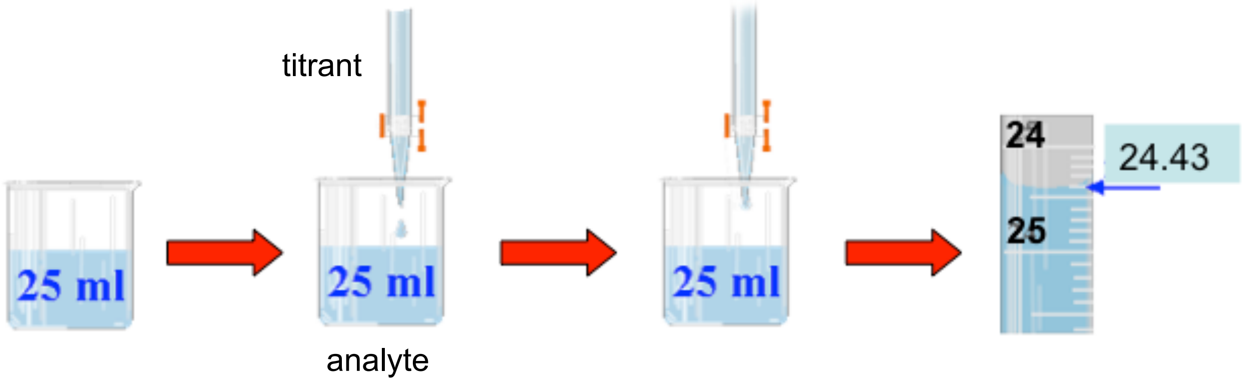
4) Redox reaction (reduction-oxidation)

$Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{3+}$

Methods of Delivering, and Measuring Titrant

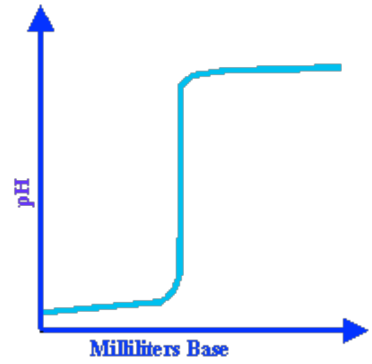
- Via a buret, volumetric titration - Majority of titrations in lab
- Using an autotitrator, volumetric
- Via a syringe, gravimetric titration

Volumetric Titrations



Need to know:

- Reaction Stoichiometry
- Titrant Concentration
- Titrant Volume



Autotitrator

- Same principles as a standard volumetric titration, but titrant is added via a calibrated motor driven delivery system.
- It is very important for the titrant delivery system to be properly calibrated.
- Also, the "detector" must also be calibrated appropriately such that the end point can be accurately determined.

Figure 11-5
Quantitative Chemical Analysis, Seventh Edition
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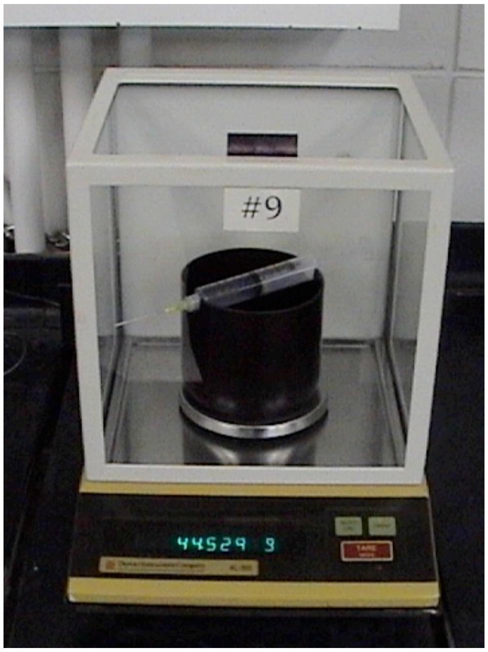
Gravimetric Titrations



- Mass of titrant delivered is determined, as opposed to volume.
- Accuracy of delivered volume is now dependent on accuracy of the balance, typically ~0.1 mg.
- 3 ppth precision with buret and 1 ppth with balance

Standards

- All our measurements are made with reference to standards
  - The accuracy of a result is only as good as the quality and accuracy of the standards used
  - A standard is a reference material whose purity and composition are well known and well defined
- Primary Standards
  - Requirements
    - High purity, at least 99.99% pure
    - Atmospheric stability, can be stored indefinitely
    - Low hygroscopicity and efflorescence
    - High solubility (for titration)
    - High formula weight so that it can be weighed with high precision
    - Modest cost
- Primary standard solutions
  - Accurately weigh primary standard and dissolve in known volume to get known concentration
    -
    -
- Secondary standard solutions
  - A solution standardized against a primary standard solution
    - Make titrant up to an approximately known concentration

- Titrate primary standard solution and use the volume required to calculate concentration of titrant
  - e.g., standardization of EDTA titrant with $CaCO_3$,
  - HCl is not a primary std since HCl slowly evaporates
  - NaOH is not a primary standard because it absorbs CO_2 to make CO_3^{2-} which changes its base strength.

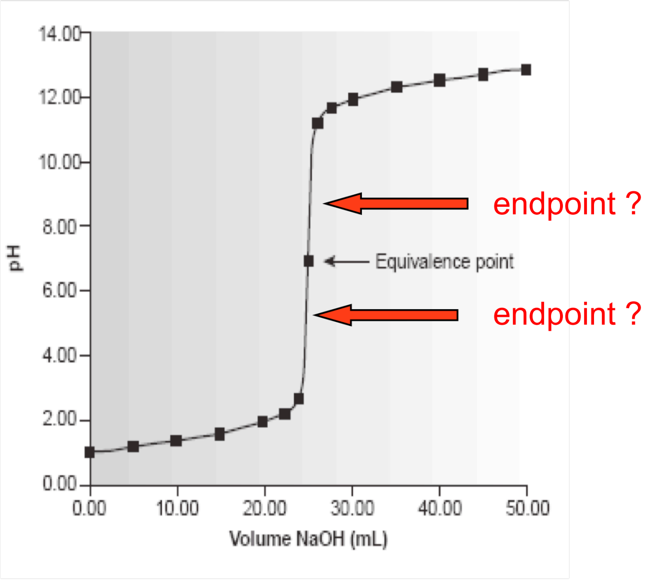
Endpoint Detection

- This is critical - if we can not see the endpoint then we do not know we have reached the equivalence point.

1) Visual indicators
   - Most common method
   - Observe a color change or precipitation at the endpoint.
     - The rxn progress may be visible directly, or an indicator may be added

2) Photometry
   - Use an instrument to follow the color change or precipitation

3) Electrochemistry
   - Potentiometry - measure voltage change such as with pH electrode
   - Amperometry - measure change in current between electrodes in solution
   - Conductance - solution conductivity changes are followed



Titration Error

- The endpoint method may not show a change exactly at the equivalence point due to the reactions involved
  - This is referred to as the titration error, calculated as
    - Error = Vol at endpoint – Vol at equivalence point
    - Negative error means endpoint is early -
    - Positive error means endpoint is late -

- Note the titration error:
  - does not refer to blunders in performing the titration (overshoot, etc.)
  -

Titration Error Correction

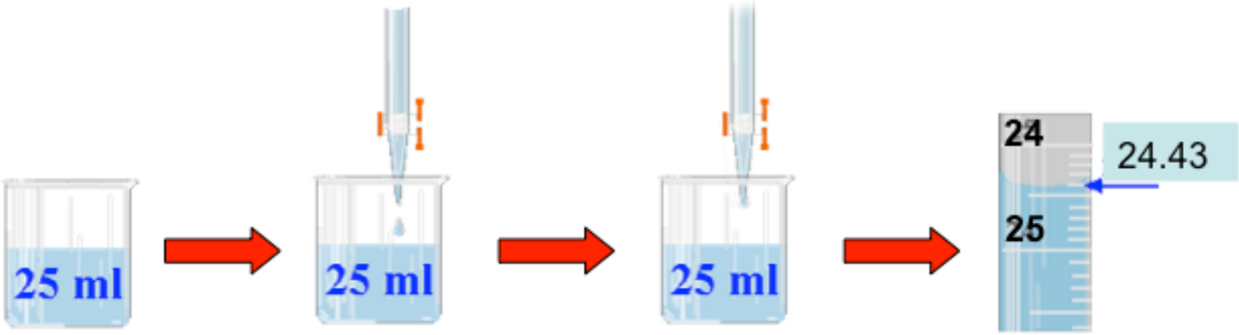
- Blank Titration
  - Same as for direct titration except a blank solution is also titrated and Vol(true titrant) = Vol(A) - Vol(blank)

Used to correct for
Impurities in buffers and reagents that react with titrant
Indicator error - consumption of titrant by the indicator
Late endpoint -

Does not correct for
Early endpoint -
Impurities in **sample** that react with titrant

Direct Titrations

- Analyte and titrant react and we observe endpoint volume
  - mol(A)/a = mol(T)/t (aA + tT → products)



Back Titrations

One of the 4 requirements of a titration rxn is not met by A + R

- Side reactions occur so we must add R quickly; or the back titration end point is easier to detect than direct titration, e.g.,

  $HSO_3^- + I_2$ (excess) $+ H_2O = SO_4^{2-} + 2I^- + 3H^+ + I_2$ (remainder)

  I_2 (remainder) $+ S_2O_3^{2-}$ = products

  We do this back titration because: $HSO_3^- + 1/2O_2 = SO_4^{2-} + H^+$ (side reaction)

  So we need to avoid this side reaction by adding the reagent (R) very quickly

Back Titration: Titrate Excess Reagent (R)

$aA + r_1R$ (in excess) = products + R_r (remainder)

r_2R_r (remainder) + tT = products [titration rxn]

- Knowing the amount of R_r (remainder) we can calculate mol(A):

  $R_r/r_2 = T/t$ R_r = mol(remaining reagent)

  $R_r = T/t \times r_2$ T = mol(titrant used)

  mol(R reacted with A) = mol(R added in excess) – mol(R_r remaining)
  = mol(R added in excess) – $T/t \times r_2$

  mol(A)/a = mol(R reacted with A)/r_1

  mol(A) = ([mol(R added) – $T/t \times r_2$]/r_1)× a

A Commercial Example of Back Titration

Kjeldahl Method: Accurate determination of nitrogen content of proteins, milk, cereal, and flour.

Discovered by **Johan Gustav Christoffer Thorsager Kjeldahl** to determine the amount of protein in grain. Apparently, less protein in grain means more beer.....

Kjeldahl worked for

Steps:
1. Digest protein in sulfuric acid
2. Neutralize the generated NH_4^+
3. Distill the NH_3 in standardized HCl
4. Back titrate the remaining HCl

Calculation Example

A 0.500 mL aliquot of protein was digested and the liberated NH_3 was distilled into 10.00 mL of 0.02140 M HCl. The unreacted HCl required 3.26 mL of 0.0198 M NaOH for complete titration. What was the original protein concentration? One mg of protein contains 0.162 mg of N in this case.

$$\text{mol}(NH_3) = ([\text{mol}(\text{HCl original}) - \text{mol T}(\text{NaOH})/t \times r_2]/r_1) \times a$$