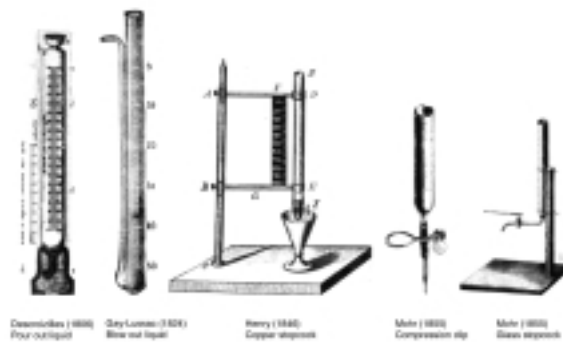


Chapter 7: Titrations

Burets Through History



Titration in Analytical Chemistry

- **Volumetric analysis** is the analytical chemistry technique where one measures the volume of reagent needed to react with the analyte
- There are some general principles that apply to all volumetric analysis procedures
- A couple specific types of titrations will be studied in this chapter.
 - Precipitation titrations
 - Spectrophotometric titrations

Titration

- The **titrant** (reagent) is added to the analyte until the reaction between them is complete.
 - Titrant is usually added using a buret.
- Assumptions in a titration:
 - The equilibrium constant is large ($K \gg 1$)
 - Reaction time is short (kinetics is fast)
- Types of titrations
 - Acid-base (Ch. 12)
 - Oxidation-reduction (Ch. 16)
 - Complex formation (Ch. 13)
 - Precipitations (Ch. 7)

End of the Analysis

- The **equivalence point** is where the quantity of added titrant has reacted stoichiometrically with the analyte.
$$5\text{C}_2\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \leftrightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$
 - 5 mol of oxalic acid reacts with 2 mol of permanganate in acidic solution
- The equivalence point is the ideal end of the titration, but what we typically measure is the **end point**, where a sudden change in a property of the solution is observed.
 - Excess MnO_4^- gives a slight purple color in solution

Process of the Titration

- Methods for determining the end point:
 - Use of an **indicator**, a compound that exhibits a property change at the endpoint (usually color)
 - Detecting a voltage change between electrodes (electrochemical)
 - Measuring a change in absorption of light (spectrophotometric)
- Error
 - The **titration error** is the difference between the end point and equivalence point
 - We try to estimate this with a **blank titration**

Calibration of the Titration

- If the titrant is prepared by dissolving pure reagent in a known volume of solution, then we can calculate its concentration and the reagent is called a **primary standard** (> 99.9% pure)
- Many reagents are not available as primary standards. In these cases we determine the concentration (**standardize**) by first titrating *against* a primary standard. The titrant is called a **standard solution**.

Types of Titration

- Titrant can be added to analyte until the reaction is complete (**direct titration**)
 - If we added MnO_4^- to oxalic acid--direct
$$5\text{C}_2\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \leftrightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$
- An excess of standard reagent can be added to analyte and the excess can be titrated with a second reagent (**indirect or back titration**)
 - If we added excess MnO_4^- to oxalic acid, and then titrated the excess MnO_4^- with Fe^{2+}

Titrimetric Analysis

- Always remember, the *key* step is to relate moles of titrant to moles of analyte
- Determination of calcium content in urine
 - 1) Ca^{2+} is precipitated as calcium oxalate

$$\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}(s)$$
 - 2) Solid is dissolved to give ions in solution

$$\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) + \text{H}_2\text{O}$$
 - 3) Standardization of permanganate solution
 - 4) Titration of oxalate with standard permanganate

$$5\text{C}_2\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \leftrightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$

Determination of Ca in Urine

- Standardization: 0.3562 g of $\text{Na}_2\text{C}_2\text{O}_4$ is dissolved in 250.0 mL water. If 10.00 mL of the solution needs 48.36 mL of KMnO_4 for titration what is the M of MnO_4^- solution?

$$M \text{Ox}^{2-} = \frac{0.3562 \text{ g Na}_2\text{C}_2\text{O}_4}{134.00 \text{ g mol}^{-1} \text{ Na}_2\text{C}_2\text{O}_4} / 0.2500 \text{ L} = 0.01063 \text{ M}$$

$$\text{moles Ox}^{2-} = (0.0163 \text{ M Ox})(0.010 \text{ L}) = 0.106 \text{ mmol}$$

$$\text{moles MnO}_4^- = \left(\frac{2 \text{ mol MnO}_4^-}{5 \text{ mol Ox}^{2-}} \right) (0.106 \text{ mmol Ox}^{2-}) = 0.04253 \text{ mmol MnO}_4^-$$

$$M \text{MnO}_4^- = \frac{0.4253 \text{ mmol MnO}_4^-}{48.36 \text{ mL}} = 8.795 \times 10^{-4} \text{ M}$$

Determination of Ca in Urine (2)

- Analysis: Calcium in a 5.00 mL urine sample was precipitated, redissolved and required 16.17 mL of standard MnO_4^- for titration
What is the concentration of Ca^{2+} ?

$$\text{moles MnO}_4^- = (0.01617 \text{ L})(8.795 \times 10^{-4} \text{ M}) = 0.01422 \text{ mmol MnO}_4^-$$

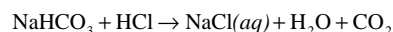
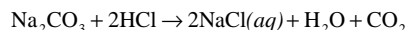
$$\text{moles Ox}^{2-} = \left(\frac{5 \text{ mol Ox}^{2-}}{2 \text{ mol MnO}_4^-} \right) (0.01422 \text{ mmol MnO}_4^-) = 0.0355 \text{ mmol}$$

$$\text{moles Ca}^{2+} = \left(\frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol Ox}^{2-}} \right) = 0.0355 \text{ mmol}$$

$$M \text{Ca}^{2+} = \frac{0.03555 \text{ mmol Ca}^{2+}}{5.00 \text{ mL}} = 0.00711 \text{ M Ca}^{2+}$$

Titration of a Mixture

- A solid mixture weighing 1.372 g contains only Na_2CO_3 and NaHCO_3 and required 29.11 mL of 0.7344 M HCl for titration:



- What is the mass of each component in the mixture?

Titration of a Mixture (2)

- $x = \text{g Na}_2\text{CO}_3$; $\text{g NaHCO}_3 = 1.372 - x$

$$\text{Moles Na}_2\text{CO}_3 = \frac{x \text{ g}}{105.99 \text{ g/mol}} \quad \text{Moles NaHCO}_3 = \frac{(1.372 - x) \text{ g}}{84.01 \text{ g/mol}}$$

$$\text{mol HCl used} = (0.02911 \text{ L})(0.7344 \text{ M}) = 0.02138 \text{ mol}$$

- From stoichiometry:

$$2(\text{mol Na}_2\text{CO}_3) + \text{mol NaHCO}_3 = 0.02138 \text{ mol}$$

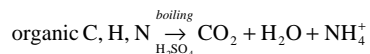
$$2\left(\frac{x}{105.99}\right) + \left(\frac{1.372 - x}{84.01}\right) = 0.02138$$

$$x = 0.724 \text{ g} = \text{Na}_2\text{CO}_3 \quad 1.372 - x = 0.648 \text{ g NaHCO}_3$$

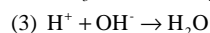
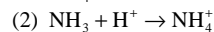
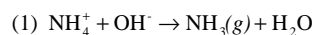
Kjeldahl Analysis

- Kjeldahl nitrogen analysis** (1883) is still commonly used for determination of nitrogen in organic substances.

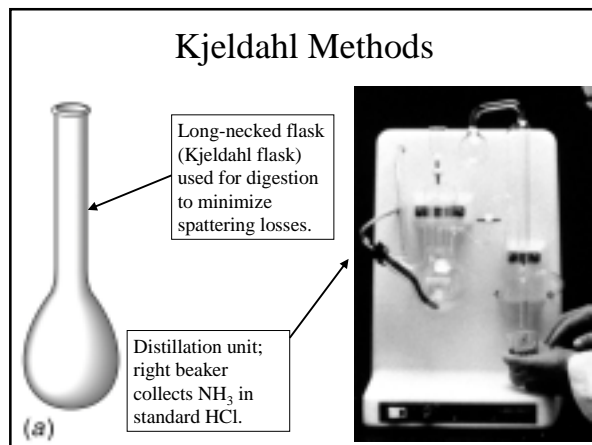
– Solid is digested (decomposed and dissolved)



– Nitrogen, as NH_4^+ , is neutralized (1) and distilled into HCl, reacting with excess HCl (2) and then excess HCl is titrated with NaOH (3)



Kjeldahl Methods



Kjeldahl Example

- A protein contains 16.2 wt% N. A 0.500 mL aliquot of protein solution was digested and liberated NH_3 was distilled into 10.00 mL of 0.02140 M HCl. Unreacted HCl needed 3.26 mL of 0.0198 M NaOH for titration. What was the concentration of protein (mg/mL)?
- How to do this?
 - 1) Total HCl present in beaker
 - 2) NaOH titrated against HCl (excess HCl)
 - 3) NH_3 reacted (Total HCl - excess HCl)
 - 4) Nitrogen in protein; mass of protein

Kjeldahl Example (2)

- Mol total HCl

$$= (10.00 \text{ mL})(0.02140 \text{ mmol/mL}) = 0.2140 \text{ mmol}$$
- Mol NaOH (mol of excess HCl)

$$= (3.26 \text{ mL})(0.0198 \text{ mmol/mL}) = 0.0645 \text{ mmol}$$
- Mol HCl used during distillation (mol NH_3)

$$= 0.2140 \text{ mmol} - 0.0645 \text{ mmol} = 0.1495 \text{ mmol NH}_3$$
- Mol N in protein = mol of NH_3 (0.1495 mmol)

$$= 0.1495 \text{ mmol N}$$

Kjeldahl Example (3)

- Mass of N in protein

$$= (0.1495 \text{ mmol})(14.00674 \text{ mg N/mmol}) = 2.093 \text{ mg N}$$
- Mass of protein

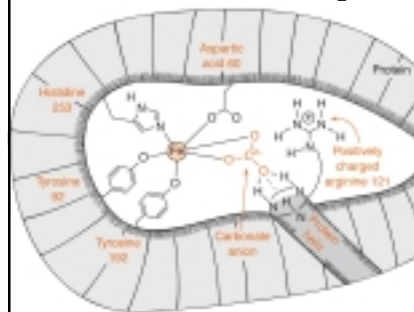
$$= \frac{2.093 \text{ mg N}}{0.162 \text{ mg N/mg protein}} = 12.9 \text{ mg protein}$$
- Concentration of protein

$$= \frac{12.9 \text{ mg protein}}{0.500 \text{ mL}} = 25.8 \frac{\text{mg protein}}{\text{mL}}$$

Spectrophotometric Titrations

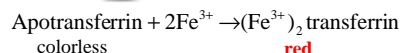
- We can use indicators to detect a color change at an endpoint, but what if we want to monitor the reaction as it takes place or if the color change is beyond the sensitivity of the human eye?
- We can use absorption of light to monitor the progress of the reaction.
 - This combines spectroscopy (Ch. 18-20) with volumetric analysis

Transferrin protein

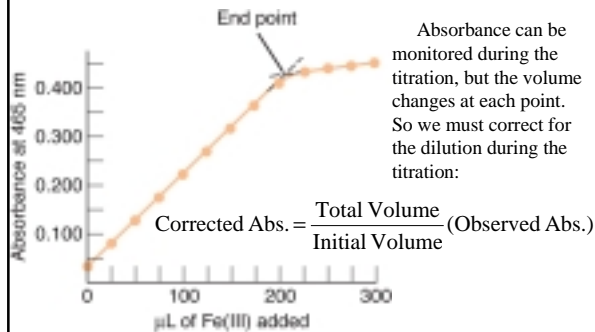


Transferrin is a protein that serves to transport iron in biochemistry. Of course, this means that transferrin can be measured by titration with iron (nitrilotriacetate).

Transferrin has a molecular mass of 81,000. Each molecule binds two iron atoms and the protein-Fe complex absorbs radiation with a maximum at 465 nm.



Titration of Transferrin with Ferric Nitrilotriacetate



Correction of Absorbance

- The absorbance measured after adding 125 μL of ferric nitrilotriacetate to 2.000 mL of apotransferrin was 0.260. What would the corrected absorbance be?

$$\text{Corrected Abs.} = \frac{2.125}{2.000} (0.260) = 0.276$$