VOLUMETRIC TITRATIONS

I. Introduction

A. Volumetric methods are one of the three categories of titrimetric methods.

B. Titrimetric methods are analytical procedures in which the amount of an analyte is determined from the amount of a standard reagent required to react completely with the analyte.

C. The three types of titrimetric methods include:
   1. Volumetric methods - measuring the volume of a solution (of known concentration) required to react completely with an analyte.
   2. Gravimetric titrimetry - measuring the mass of a known reagent required to react completely with an analyte.
   3. Coulometric titrimetry - measuring the electrical current (amps) produced when a known amount of reagent reacts completely with an analyte.

II. Terminology of Volumetric Titrimetry.

A. Standard solution (or standard titrant) - a reagent used to titrate the analyte. The reagent must:
   1. Have a precisely known concentration.
   2. Generally is added from a buret.

B. Equivalent point - point in a titration where the added titrant is chemically equivalent to the analyte (i.e., reaction is at the stoichiometric ratio).

C. End Point - a physical property (e.g., a color change) associated with the end point that it used to stop the titration.

D. Titration error - the difference in added titrant volume between the end point and the equivalence point.

\[ E_{\text{titration}} = V_{\text{end point}} - V_{\text{equivalence point}} \]

E. Indicator - a species added to the analyte to give an observable change (which is the end point) at or near the equivalence point.

F. Back-titration - titrating the amount of excess titrant added using a second standard titrant.

G. Primary standard - a highly purified compound that serves as a reference material.
   1. Desired properties of the primary standard include:
      a. High purity.
      b. Stability in air.
      c. Absence of hydrated water molecules.
      d. Moderate cost and easy availability.
      e. Solubility in the titration solutions.
      f. Large formula weight (molecular weight), since this minimizes weighing errors.

   2. Compounds used as standards that do not meet all these criteria are called secondary standards.
3. Some commonly used primary standards include:

a. Potassium hydrogen phthalate (KHP) (Molec. Wt. 204.223) - The pure compound is dried at 105°C and used to standardize base using phenolphthalein as an indicator.

b. Hydrochloric Acid (Molec. Wt. 36.461) - HCl and water distill as an azeotrope whose composition (~6 M) is pressure dependent. The composition is tabulated in references.

c. Potassium hydrogen iodate (KH(IO₃)₂) (Molec. Wt. 389.912) - Strong acid for standardizing bases. Any indicator with an endpoint between pH 5-9 may be used.

d. Sodium carbonate (Na₂CO₃) (Molec. Wt. 105.989) - Purchased as primary standard grade commercially. Recrystallized NaHCO₃ may be heated for 1 hour at 265°C to produce pure Na₂CO₃. Sodium carbonate is titrated with strong acid to an end point of pH 4-5.

III. Standard Solutions.

A. Standard solutions are central to all volumetric methods.

B. The standard solution is used to react with the analyte, and all stoichiometric calculations are dependent on the accurate measurement of the volume of standard solution reacted.

C. Standard solutions are prepared in two ways:

1. Direct method - a primary standard compound is carefully weighed and dissolved in an exactly known volume of solution. The direct method is the best method to utilized.

2. Standardization - the prepared standard solution is standardized by using it to titrate...

   a. A carefully weighed primary standard compound.

   b. A carefully weighed secondary standard compound.

   c. A carefully measured volume of another standard solution.

3. If the standard solution is standardized against another standard solution or a secondary standard, it is sometimes called a secondary standard solution.

D. Desirable properties of the standard solution include:

1. The solution is stable and does not require re-standardization before use.
2. The standard solution reacts quickly with the analyte.
3. The reaction with the analyte is complete and a good endpoint is observed.
4. The reaction with analyte is selective and described by a simple, balanced equation.

IV. Review of Volumetric Calculations.

A. Mole calculations:

moles of species X = [# grams X]/[Molar Mass of X]

moles of X = [Volume (in liters)] [Molarity]

For dilutions, 

( [Volume] [Molarity] ) before dilution = ( [Volume] [Molarity] ) after dilution
B. Sample calculations: **TO BE DONE IN CLASS!**

1. Describe the preparation of 900.0 mL of 0.0450 M KOH from a 50.0% stock KOH solution (specific gravity of the stock solution = 1.505).

2. A Ba(OH)\(_2\) solution was standardized using benzoic acid. In the titration, 34.72 mL of the Ba(OH)\(_2\) solution was required to titrate 0.1036 grams of benzoic acid.
   a. What is the molarity (M) of the barium hydroxide solution?
   b. Calculate the absolute standard deviation of the titration results if the standard deviation of the weighing was +/- 0.23 mg and the standard deviation of the volume measurement was +/- 0.31 mL.
   c. Assuming an error of -0.32 mg in the weighing of benzoic acid, calculate the absolute and relative systematic error in these titration results. (Assume the determinate error in the volume measurements to be zero.)

V. Titration Curves: An Overview

A. A titration curve is a plot of reagent volume (e.g., mL of AgNO\(_3\) solution added) versus some function of the analyte concentration.

1. Volume of added reagent is generally plotted on the x axis.
2. The measured parameter that is a function of analyte concentration is plotted on the y axis.

B. 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.
   a. The equivalent point is observed in the middle of the "middle" segment of the "z" or "s."
   b. A large number of measurements are made near and surrounding the equivalence point.
2. Linear-segment curve - a curve generally consisting of two line segments that intersect at an angle.

![Graph showing linear-segment curve]

a. Measurements are often made well away from the equivalence point (where the reaction is nearly complete), and the lines are extrapolated to intersection.

b. The equivalence point is generally associated with the intersection of the line segments.

3. The vast majority of titrations follow a sigmoidal curve, and we will deal exclusively with that type.

VI. A Typical Titration: Strong Acid (HCl) Titrated With Strong Base (NaOH)

A. Consider a hypothetical titration of a 50.00 mL aliquot of 0.1000 M HCl with 0.1000 M NaOH.

\[ \text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl} \]

Or, written as a net ionic equation:

\[ \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2 \text{H}_2\text{O} \]

1. The progress of the titration can be followed as a function of pH or pOH.

![Graph showing pH and pOH as functions of volume of reagent]
2. Since the acid and base have the same concentration, it is correctly assumed that 50.00 mL of NaOH solution will be required to reach equivalence.

![Graph showing pH vs. Volume of Reagent (mL)]

a. Note that during titration, little change occurs up to about 40.0 mL. pH remains constant, despite the fact that a lot of base has been added.

b. Near the equivalence point, tiny volumes of added NaOH made huge changes in pH.

1) Note that from 49.99 mL to 50.00 mL a pH 5.0 to pH 7.0 jump occurred.
2) From 50.00 mL to 50.01 mL a pH 7.0 to pH 9.0 jump occurred.

c. Past the equivalence point, large additional volumes of NaOH make little difference in pH. The pH asymptotically approaches the pH of 0.1000 M NaOH.

d. Note that the titration can be plotted as a function of pH or pOH.

e. Indicators must change color abruptly in the equivalence region to be of use (typically 1-2 pH units). In this case, any indicator that changes +/- 2 pH units of 7 will work.