Volumetric Titration

Titration in Analytical chemistry

Titrations are widely used in analytical chemistry to determine acids, bases, oxidants, reductants, metal ions, proteins, and many other species. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry. The volume, or the mass, of the titrant needed to react completely with the analyte is
determined and used to calculate the quantity of analyte.
A volume-based titration is shown in this figure in which the standard solution is added from a buret, and the reaction occurs in the Erlenmeyer flask.

In some titrations, known as coulometric titrations, the quantity of charge required to completely consume the analyte is obtained. In any titration, the point of chemical equivalence, called the end point when determined experimentally, is signaled by an indicator color change or a change in an instrumental response.
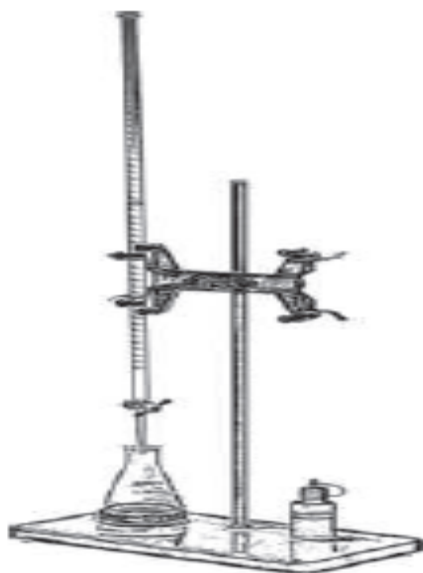
Figure in which the standard solution is added from a buret, and the reaction occurs in the Erlenmeyer flask.

Volumetric Titration

Titration methods are based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte. The reagent may be a standard solution of a chemical or an electric current of known magnitude.

In **volumetric titrations**, the volume of a standard reagent is the measured quantity.

In **coulometric titrations,** the quantity of charge required to complete a reaction with the analyte is the measured quantity.

Some Terms Used in Volumetric Titrations

A **standard solution** is a reagent of known concentration. Standard solutions are used in titrations and in many other chemical analyses.

The _ideal_ standard solution for a titrimetric method will
1. be sufficiently stable so that it is necessary to determine its concentration only 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 a balanced

Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution. Back-titrations are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability.

Volumetric Titration

The **equivalence point** is the point in a titration when the amount of added standard reagent is equivalent to the amount of analyte.

The **end point** is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

 Titration error In volumetric methods, the, E_t, is given by

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

Where V_{ep} is the actual volume of reagent required to reach the end point and V_{eq} is the theoretical volume necessary to reach the equivalence point

A **primary standard** is an ultrapure compound that serves as the reference material for a titration or for another type of quantitative analysis.

Important requirements for a primary standard are the following:

1. High purity. Established methods for confirming purity should be available.
2. Atmospheric stability.
3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
4. Modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

A **secondary standard** is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

In a **standardization,** the concentration of a volumetric solution is determined by titrating it against a carefully measured quantity of a primary or secondary standard or an exactly known volume of another standard solution.

Volumetric Titration

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13C VOLUMETRIC CALCULATIONS

As we indicated in Section 4B-1, we can express the concentration of solutions in several ways. For the standard solutions used in most titrations, either **molar concentration**, c, or **normal concentration**, c_N, is usually used. Molar concentration is the number of moles of reagent contained in one liter of solution, and normal concentration is the number of **equivalents** of reagent in the same volume.

Throughout this text, we base volumetric calculations exclusively on molar concentration and molar masses. We have also included in Appendix 7 a discussion of how volumetric calculations are performed based on normal concentration and equivalent masses because you may encounter these terms and their uses in the industrial and health science literature.

13C-1 Some Useful Relationships

Most volumetric calculations are based on two pairs of simple equations that are derived from definitions of the mole, the millimole, and the molar concentration. For the chemical species A, we can write

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} \tag{13-1}$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}} \tag{13-2}$$

The second pair of equations is derived from the definition of molar concentration, that is,

$$\text{amount A (mol)} = V\,(\text{L}) \times c_A \left(\frac{\text{mol A}}{\text{L}}\right) \tag{13-3}$$

$$\text{amount A (mmol)} = V\,(\text{mL}) \times c_A \left(\frac{\text{mmol A}}{\text{L}}\right) \tag{13-4}$$

where V is the volume of the solution.

Equations 13-1 and 13-3 are used when volumes are measured in liters, and Equations 13-2 and Equations 13-4 when the units are milliliters.

EXAMPLE 13-2

A standard 0.0100 M solution of Na^+ is required to calibrate an ion-selective electrode method to determine sodium. Describe how 500 mL of this solution can be prepared from primary standard Na_2CO_3 (105.99 g/mL).

Solution

We wish to compute the mass of reagent required to produce a species concentration of 0.0100 M. In this instance, we will use millimoles since the volume is in milliliters. Because Na_2CO_3 dissociates to give two Na^+ ions, we can write that the number of millimoles of Na_2CO_3 needed is

$$\text{amount } Na_2CO_3 = 500 \text{ mL} \times \frac{0.0100 \text{ mmol } Na^+}{\text{mL}} \times \frac{1 \text{ mmol } Na_2CO_3}{2 \text{ mmol } Na^+}$$

$$= 2.50 \text{ mmol}$$

From the definition of millimole, we write

$$\text{mass } Na_2CO_3 = 2.50 \text{ mmol } Na_2CO_3 \times 105.99 \frac{\text{mg } Na_2CO_3}{\text{mmol } Na_2CO_3}$$

$$= 264.975 \text{ mg } Na_2CO_3$$

Since there are 1000 mg/g, or 0.001 g/mg, the solution should be prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.

13C-2 Calculating the Molar Concentration of Standard Solutions

The following three examples illustrate how the concentrations of volumetric reagents are calculated.

EXAMPLE 13-1

Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary-standard-grade solid.

Solution

$$\text{amount } AgNO_3 = V_{soln}(L) \times c_{AgNO_3}(mol/L)$$

$$= 2.00\ L \times \frac{0.0500 \text{ mol } AgNO_3}{L} = 0.100 \text{ mol } AgNO_3$$

To obtain the mass of $AgNO_3$, we rearrange Equation 13-2 to give

$$\text{mass } AgNO_3 = 0.1000 \text{ mol } AgNO_3 \times \frac{169.87 \text{ g } AgNO_3}{\text{mol } AgNO_3}$$

$$= 16.987 \text{ g } AgNO_3$$

Therefore, the solution should be prepared by dissolving 16.987 g of $AgNO_3$ in water and diluting to the mark in a 2.000 L volumetric flask.

EXAMPLE 13-3

How would you prepare 50.0-mL portions of standard solutions that are 0.00500 M, 0.00200 M, and 0.00100 M in Na^+ from the solution in Example 13-2?

Solution

The number of millimoles of Na^+ taken from the concentrated solution must equal the number in the dilute solutions. Thus,

$$\text{amount } Na^+ \text{ from concd soln} = \text{amount } Na^+ \text{ in dil soln}$$

Recall that the number of millimoles is equal to the number of millimoles per milliliter times the number of milliliters, that is,

$$V_{concd} \times c_{concd} = V_{dil} \times c_{dil}$$

where V_{concd} and V_{dil} are the volumes in milliliters of the concentrated and diluted solutions, respectively, and c_{concd} and c_{dil} are their molar Na^+ concentrations. For the 0.00500-M solution, this equation can be rearranged to

$$V_{concd} = \frac{V_{dil} \times c_{dil}}{c_{concd}} = \frac{50.0 \text{ mL} \times 0.005 \text{ mmol Na}^+/\text{mL}}{0.0100 \text{ mmol Na}^+/\text{mL}} = 25.0 \text{ mL}$$

Therefore, to produce 50.0 mL of 0.00500 M Na^+, 25.0 mL of the concentrated solution should be diluted to exactly 50.0 mL.

Repeat the calculation for the other two molarities to confirm that diluting 10.0 and 5.00 mL of the concentrated solution to 50.0 mL produces the desired concentrations.