

Chapter 9 Titration

A titration is a method of determining the unknown concentration of a substance by reacting it with a known chemical substance.

A titration requires

1. the reaction between the chemicals to be rapid and complete.
2. few competing reactions
3. the exact quantities of one of the reactants to be known.

There are several types of titrations but the two most common titrations are acid/base titrations and oxidation/reduction titrations.

Titration Theory

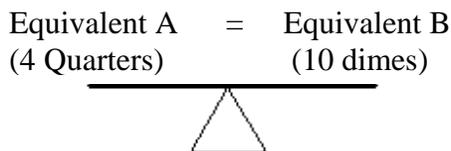
Analytically, all titrations are the same.

A titration occurs when a chemical called a titrant is placed in a buret. The unknown sample is placed in a beaker or Erlenmeyer flask. A chemical called an indicator is added to the unknown solution and stirred.

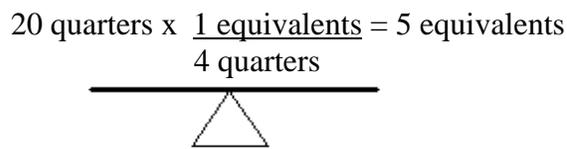
As the stopcock on the buret is opened, the titrant is added, the unknown sample begins to react with the titrant. The titrant continues to be added until the indicator changes to the expected color. The color change indicates the teeter totter is balanced and the endpoint reached. The endpoint indicates an equivalent amount of titrant and sample have been added and the reaction is complete. The unknown concentration can now be calculated.

Equivalents

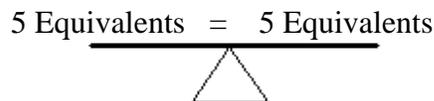
The titration is essentially a chemical balancing act.



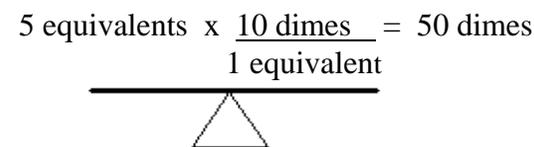
When the equivalents of A equal the equivalents of B, the teeter totter will be balanced and the equivalence point is reached. For example, if 4 quarters are placed on the left side of the teeter totter, 10 dimes could be placed on the right side of the teeter totter. Even though both sides don't weigh the same, they are equivalent because they would both purchase a \$1 hamburger. We could then say 4 quarters is equivalent to \$1. If one equivalent is \$1, how many equivalents would be present if the left side of the teeter totter has 20 quarters?



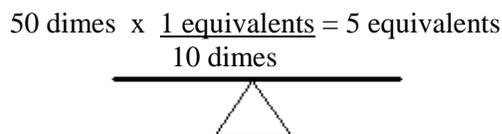
How many equivalents would it take to balance the teeter totter?



How many dimes would it take to have 5 equivalents on the right side?



If 37 pesos equals \$1, how many pesos would it take to balance 50 dimes?



$$5 \text{ equivalents} \times \frac{37 \text{ pesos}}{1 \text{ equivalent}} = 185 \text{ pesos}$$


By using equivalents in a titration, chemical reactions do not need to be balanced or even understood. In a titration, equivalents are hidden in the term Normality, N. By definition a 1 N solution contains 1 equivalent per liter, therefore, a 0.02 N solution would contain 0.02 equivalents per liter.

Standardization

The first step in a titration is the standardization of the titrant. When performing a titration, one side of the teeter totter always needs to be known. By convention, this is usually the solution in the buret. This solution can be prepared or purchased. In either case, the concentration of the titrant must be known or verified if purchased. To standardize the titrant, a primary standard is used. A primary standard is a solution that has special characteristics. The most important characteristics of a primary standard are

1. stable to light. The standard does not change concentration when exposed to light
2. stable to temperature. The standard does not change concentration when exposed to an increase or decrease in temperature.
3. doesn't absorb moisture when weighed (not hygroscopic). This is very important when preparing in-house standards.

In most cases, it is best to purchase primary standards from a reputable supplier than to prepare them in-house.

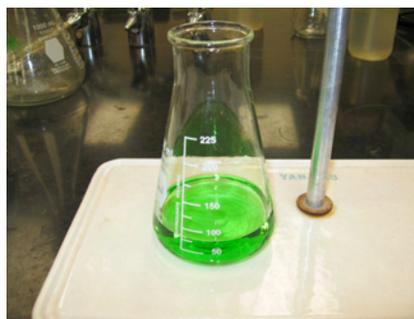
For example, let's purchase a 0.02 N primary standard solution of sodium carbonate. The 0.02 N indicates the bottle has a concentration of 0.02 equivalents of sodium carbonate per liter. Now pipet 20.0 ml of the sodium carbonate standard solution into a 100 ml Erlenmeyer flask. The flask now contains 0.0004 equivalents of sodium carbonate.

$$\frac{0.02 \text{ equivalents}}{1 \text{ liter}} \times \frac{1 \text{ liter}}{1000 \text{ ml}} \times 20 \text{ ml} = 0.0004$$

One side of the teeter totter is now known.

$$0.0004 \text{ equivalent} = \text{Equivalent B}$$

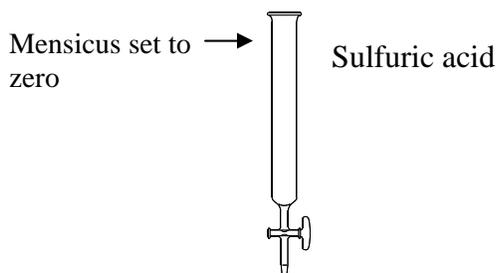

A few drops of methyl purple indicator is added to the sodium carbonate to create a green color.



The right side of the teeter totter is the solution that needs to be standardized. In this example, sulfuric acid will be on the right side of the teeter totter and in the buret. Once we standardize the sulfuric acid it can be used to determine the alkalinity of the anaerobic digester.

The buret is filled from a bottle of sulfuric acid that has been sitting on the shelf for 3 months. The bottle is labeled 0.02 N but since the sulfuric acid is not a primary

standard it must be periodically standardized since it may have deteriorated. First, remember to rinse the buret with small amounts of the sulfuric acid. Bleed the buret tip to remove bubbles, then adjust the meniscus to zero.



The titration now begins as the sulfuric acid is "titrated" into the Erlenmeyer flask. The sulfuric acid titrant should be added as quickly as possible without passing the endpoint and should be swirled to quickly complete the reaction. The flask can be swirled by hand or more conveniently stirred using a magnetic stirrer. If using the magnetic stirrer, the magnetic will be placed in the Erlenmeyer flask and the speed adjusted to mix quickly without splashing the solution onto the side of the flask.

In this example, the endpoint will be purple. As the sulfuric acid is added, the solution in the Erlenmeyer flask will flash purple as the titrant is added. The color will quickly return to green. As the teeter totter comes closer to balancing, (reaching the equivalence point), the purple color will last longer and longer. At this point the addition of the sulfuric acid should be slowed to a drop at a time.



When the purple color finally persists, the equivalence point has been reached, the teeter totter balanced and the standardization is complete. Record the volume of sulfuric acid that was added from the buret.

Calculations

All titrations use the same basic formula

$$\text{Concentration A} \times \text{Volume A} = \text{Concentration B} \times \text{Volume B}$$

Notice how the formula sets up like the teeter totter. In this example, 20.0 ml of 0.02 N sodium carbonate was used and titrated to the purple endpoint using 24.2 ml of sulfuric acid.

$$0.02 \text{ N} \times 20.0 \text{ ml} = \text{Sulfuric acid concentration} \times 24.2 \text{ ml}$$

Solve the equation to determine the acid concentration.

$$\frac{0.02 \text{ N} \times 20.0 \text{ ml}}{24.2 \text{ ml}} = \text{Sulfuric acid concentration}$$

$$0.017 \text{ N} = \text{Sulfuric acid concentration}$$

The sulfuric acid that has been sitting for 3 months has now been standardized. Notice that the concentration from a bottle labeled 0.02 N has deteriorated over the past 3 months to an actual concentration of 0.017N. This decay is why standardization

is essential. All data generated during the past 3 months is invalid.

Quality Control

How often should titrants be standardized? There is no uniform answer since all titrants do not have the same stability. The best answer is that standardization should be performed frequently. If the concentration changes between standardizations, all data generated after the last standardization becomes invalid. If the sulfuric acid just standardized had been used during the past three months rather than just sitting on the shelf, any results generated would be incorrect since the normality was incorrect.

Performing the standardization is only half the job. All the standardization information must be recorded.

QC Record the lot number, expiration date, purchase date, concentration of the primary standard

QC Record the date and time of the standardization

QC Record the name of the analyst

Additional tips

Some endpoints are difficult to determine. Going past the endpoint by adding more sulfuric acid than necessary will unbalance the teeter totter and give erroneous results. When in doubt, note the buret reading, then add another drop or two. If the color still changes, continue adding a drop at a time until the color persists. If the color does not show any change, use the previous buret reading.

A sheet of white paper placed below the beaker or flask can sometimes help visualize the endpoint color.

A drop of titrant on the tip of the buret is an error. Once the drop has left the buret, the

drop has been added to the solution as far as the buret reading is concerned. The drop can be added to the solution by using a DI water squirt bottle to rinse it into the Erlenmeyer flask.

Always validate the normality of a purchased standard and re-standardize any time new reagents are prepared. In this example, the only prepared reagent is the methyl purple indicator. If a new batch has been prepared, re-standardize the sulfuric acid.

Sample Determination

Now that the sulfuric acid has been standardized, it can be used to measure something else. Lets measure the alkalinity of the anaerobic digester.

Since the sulfuric acid is still in the buret, leave it there. Pipet 25.0 ml of separated digester supernatant into an Erlenmeyer flask, add the stirring bar and a few drops of indicator. Titrate to the purple endpoint by again adding the sulfuric acid quickly then slowing until the endpoint is reached. The endpoint is reached after 39.6 ml of sulfuric acid was added. (Remember to stop the buret at the 25 ml mark then refill!!)

$$\text{Sample concentration} \times 25.0 \text{ ml} = 0.017 \text{ N sulfuric acid} \times 39.6 \text{ ml}$$

Notice, the standardized sulfuric acid concentration (0.017N) is now used in the calculations. Solve.

$$\begin{aligned} \text{Sample concentration} &= \frac{0.017 \text{ N sulfuric acid} \times 39.6 \text{ ml}}{25.0 \text{ ml}} \\ &= 0.027 \text{ N} \end{aligned}$$

The sample alkalinity can now be reported as 0.027 N. However, normality is not a common concentration unit for most

wastewater analysis. The most common unit to report alkalinity concentration is mg/L. In this example, normality can be converted to mg/L by multiplying by 50,000. Changing from N to mg/L could be compared to converting dollars into pesos.

$$0.027 \text{ N} \times \frac{50,000 \text{ mg/L}}{1 \text{ equivalent}} = 1350 \text{ mg/L}$$

Standard Methods contains many titration procedures but they all follow the same general principles described above.

