

TITRIMETRIC ANALYSIS

INTRODUCTION

- Titrimetric analysis (Titration) is one of the core and the most useful analytical procedures that make up quantitative techniques in analytical chemistry.
- Titrimetric analysis involves determination of the volume of a solution of accurately known concentration, which is required to react quantitatively with the measured volume of the solution of a substance, concentration of which is to be determined.
- The technique of volumetric analysis is the simplest type of titrimetry, and involves the addition of controlled volumes of a reagent solution, the **titrant**, to a known volume of another solution, the **titrand** in a volumetric titration.
- Titrant is usually added from burette to the titrand or the analyte in a conical flask.
- **Titration** is a method used to determine the concentration of an unknown sample solution by a known concentration of solute.

Requirement For a Reaction in The Titrimetric Analysis

- The titration reaction should have large equilibrium constant i.e. each addition of titrant must be completely used up by the analyte.
- The reaction must be rapid.
- There should be known reaction pattern between the analyte and titrant
- There should be no side or parallel reaction i.e. the reaction should be specific with no interference.
- The reaction should be quantitative.
- There should be distinct features in some property of the solution when the reaction is complete.
- The end point should coincide with the equivalence point and be reproducible.

Various Technical Terms in Volumetric Analysis

- **Indicator:** is a compound with a physical property (colour) which changes abruptly near the equivalence end point. At the completion of the reaction, the indicator shows a visible change e.g. (colour change or turbidity) in the solution being titrated. An indicator is chosen in a particular titration based on the pH-range of the indicator and the pH change near the equivalence point.
- **Standardization:** is a process by which the precise concentration of a solution is determined.
- **Standard Solution:** A solution of exactly known concentration is called standard solution. Any substance, which is stable at room temperature and does not react with solvent in which it is dissolved, can be directly weighed to prepare its standard solution.
- **Primary Standard:** A primary standard is a compound of sufficient purity in which total amount of impurities does not exceed 0.01-0.02%. It is used to prepare a standard solution. The purity is above 99.9%. A primary standard should be easy to obtain, dry, stable and not hygroscopic, but should be readily soluble and react rapidly and stoichiometrically. They should ideally have a high relative molecular mass to minimize weighing errors.
- **Secondary Standard:** A solution of secondary standard is the one which may be used for standardization after finding out its exact concentration by titration against a standard solution of primary standard. A secondary standard cannot be used for preparing standard solution by direct weighing. Sodium hydroxide and potassium permanganate are examples of secondary standards.

- **Equivalence point:** This is the point in which the quantity of titrant added is the exact amount necessary for stoichiometric reaction with the analyte or the titrand. It is the theoretical amount of solution that must be added until the reaction is just complete.
- **End-point:** This is the actual point when a reaction is observed to be complete. the end point in a titration is the point at which change is detected accurately.
- **Titration Error:** It is sometimes called indicator error, if indicator is used as a means of detecting end point. In an ideal titration, the visible end point coincides with the stoichiometric or theoretical end point; but in practice usually some small difference occurs. This represents titration error. Indicator and the experimental conditions selected should be such that the difference between the visible end point and the theoretical end point is minimum.
- **Blank titration:** It is the type of titration in which the solution does not contain the analyte of interest. It is always carried out to estimate the amount of titration error.
- **Direct titration:** Is the most common form of titration in which titrant is added to the analyte until reaction is complete.
- **Back titration:** It is the type of titration necessary when direct titration does not give clear or sharp end point. It involves adding a known excess of the standard reagent to the analyte. Then a second standard reagent is used to titrate the excess of the first reagent so as to know the amount of first standard reagent that is consumed by analyte.

Titrimetric Calculation

- In quantitative estimation through titrimetric analysis, concentration of solution is expressed in terms of molarity. It is number of moles of solute dissolved in 1 litre of solution.

- *Molarity, $M = \frac{\text{number of moles of solute}}{\text{volume of solution in litres}}$*

- A molar solution contains 1 mole of solute per 1000 cm^3 (or 1 L) of solution. Therefore, 1 cm^3 of a 1 M solution contains 1 mmol of solute.

- *$Mole = \frac{Mass}{Molar\ mass}$*

- **Example 1**

A 25.00 cm^3 aliquot of a solution of a base of known concentration 0.1057 M is titrated with an acid of unknown concentration. The reaction involved 1 mole of base and 1 mole of acid. The end point was determined as 24.88 cm^3 of acid added. What is the concentration of the acid?

- **Solution**

25.00 cm^3 of the base solution contained $25.00 \times 0.1057 = 2.6425$ mmol base.

From the known reaction, this should be equivalent to 2.6425 mmol of acid.

Since the volume of acid at the end point was 24.88 cm^3 , the concentration must be $(2.6425/24.88) = 0.1062$ M.

- **Class work**

How many millilitres of 0.25 M of H_2SO_4 will react with 10 ml of a 0.25 M solution of NaOH ?

Types of Volumetric Procedures.

- Acid-Basic titration
- Oxidation- reduction (redox) titration
- Precipitation titration
- Complexometric titration

Acid-Base titration

- Acid-Base titrations or neutralization titrations are usually used to find the appropriate amount of a known acidic or basic substance through acid-base reactions. In an acid-base titration, one of the solutions is an acid and the other a base. **Acids** are those substances which have sour taste, sharp odor, corrosive, having $\text{pH} < 7$ and turn blue litmus red. The neutralization reaction occurs when acid reacts with alkali, forms salt and water. **Bases** are those substances which have bitter taste, odorless, turn red litmus blue, having pH more than 7 and becomes less alkaline when react with acid.

Applications for acid-base titrations

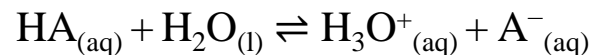
- Determination of innumerable inorganic, organic and biological species that possess inherent acidic or basic properties.
- The determination of the concentration of acid in foods and pharmaceuticals.
- The measurement of acid number (or base number) during the course of a reaction. For example, in the production of polyester resins by the reaction of a glycol with maleic and phthalic acids, the total acid remaining is determined by titration of a weighed sample with potassium hydroxide using phenolphthalein as indicator.
- The Kjeldahl method for nitrogen determination is a good example of a back titration. The sample (for example, a food product) is oxidized by concentrated sulfuric acid to remove carbonaceous matter. Excess sodium hydroxide solution is then added, and the ammonia released is carefully distilled off into a known volume of standard acid, such as 0.1 M boric acid. The excess acid is then titrated with standard alkali.

THEORIES OF ACIDS AND BASES

- **Arrhenius theory** which describes an acid as any substance that ionizes partially or completely in water to give hydrogen ion, while base is any substance which ionizes partially or completely in water to give hydroxyl ions. According to the **Arrhenius concept** of acids and bases, an acid is a substance that, when dissolved in water, increases the concentration of hydronium ion (H_3O^+). A base, in the Arrhenius concept, is a substance that, when dissolved in water, increases the concentration of hydroxide ion, OH^- .
- **Bronsted-lowry theory** describes an acid as a substance that can donate a proton and a base as any substance that can accept a proton. From here, we can note that when an acid reacts with a base, the proton is transferred from one chemical species to another.
- **Lewis acid-base theory**: According to this theory, an acid is a substance which has capability to accept the non-bonding pair of electrons, called Lewis acid. A base is a substance which has capability to donate the electrons, called Lewis base.

Relative Strengths of Acids and Bases

- The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed strong; if relatively little ionization occurs, the acid or base is weak.
- The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a .
- For the reaction of an acid HA:



The acid ionization constant is written

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

where the concentrations are those at equilibrium.

- Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\text{H}_2\text{O}]$ in the equation.
- Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{(\text{eq})}}{[\text{HA}]_0} \times 100$$

- Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases.

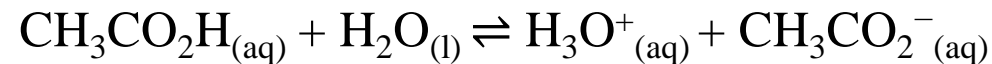
Determination of K_a from Equilibrium Concentrations

- **Example**

Acetic acid is the principal ingredient in vinegar that provides its sour taste. At equilibrium, a solution contains $[\text{CH}_3\text{CO}_2\text{H}] = 0.0787 \text{ M}$ and $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CO}_2^-] = 0.00118 \text{ M}$. What is the value of K_a for acetic acid?

- **Solution**

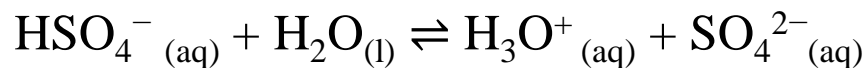
The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_a for acetic acid.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{(0.00118)(0.00118)}{(0.0787)} = 1.77 \times 10^{-5}$$

- **Class Exercise**

The HSO_4^- ion, weak acid used in some household cleansers:



What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition: $[\text{H}_3\text{O}^+] = 0.027 \text{ M}$; $[\text{HSO}_4^-] = 0.29 \text{ M}$; and $[\text{SO}_4^{2-}] = 0.13 \text{ M}$?

Calculation of Percent Ionization from pH

Example

Calculate the percent ionization of a 0.125-M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{(eq)}}{[HA]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[H_3O^+] = 10^{-2.09} = 0.0081 \text{ M}$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Class Exercise

Calculate the percent ionization of a 0.10-M solution of acetic acid with a pH of 2.89.

Relative Strength Of a Base

- Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions.
- In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases.
- A stronger base has a larger ionization constant than does a weaker base.

• For the reaction of a base, B:



- The ionization constant is written as

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

where the concentrations are those at equilibrium.

- Again, we do not include $[H_2O]$ in the equation because water is the solvent.

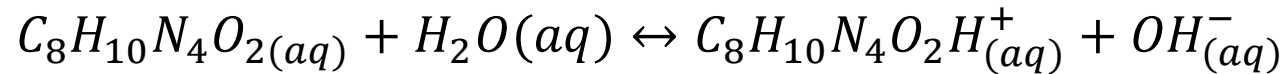
Determination of K_b from Equilibrium Concentrations

- **Example**

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050 M$, $[C_8H_{10}N_4O_2H^+] = 5.0 \times 10^{-3}M$, and $[OH^-] = 2.5 \times 10^{-3}M$?

- **Solution**

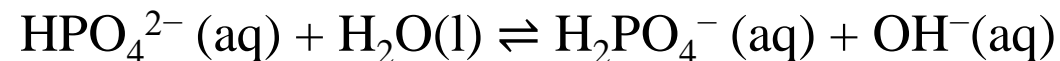
At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:



$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

- **Class Exercise**

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:



$[OH^-] = 1.3 \times 10^{-6}M$; $[H_2PO_4^-]=0.042M$; and $[HPO_4^{2-}]=0.341M$

Oxidation- reduction (redox) titration

- Oxidation – Reduction reaction is a reaction which involves the movement of electrons from one point to another, in a reaction between analyte and titrant.
- Oxidation-reduction or redox titrations are used for determining metals with two well-defined oxidation states, and indirect methods for the determination of organic compounds.
- The general principle of Redox reaction lies in the fact that reaction occurs between a reducing and an oxidizing agent.
- **Oxidation** is simply defined as loss of electron to give higher oxidation state. The electrode is always more positive.
- **Reduction** is defined as gain of electron to give lower oxidation state. The reduction electrode is always more negative.
- **Oxidizing agent** is the substance (s) that tend to take up an electron(s) and get reduced to lower oxidation state. Examples of oxidizing agents include Permanganate compounds such as potassium permanganate ($KMnO_4$), Halogens such as fluorine (F_2) and chlorine (Cl_2), sodium dichromate, hydrogen peroxide (H_2O_2), potassium nitrate (KNO_3).
- **Reducing agent** is the substance(s) that tend to give up electron(s) and get oxidized to higher oxidation state. Examples of reducing agents include Lithium aluminium hydride ($LiAlH_4$), Sodium borohydride, Oxalic acid, Diborane, Sodium lead alloy.

Indicators For Redox Reactions

- The indicators for redox reactions are reagents whose oxidized and reduced forms differ in color.
- Three visual indicators are commonly used.
 - **Self indicator** This is when the titrant is highly colored .The colour change may be used to detect the end point. Example: Titration of acidified $KMnO_4$ against freshly prepared $FeSO_4$ solution. $KMnO_4$ which is deep blue/pink converts to colorless at end point.
 - **Starch indicator:** One further useful indicator employed in redox titrations involving iodine is starch, or more synthetic equivalent materials. The starch forms a blue-black complex with iodine, which is rendered colorless when all the iodine has been removed.
 - **Redox Indicators:** These are highly colored dyes. They are weak reducing or oxidizing agent. Example is Ferroin whose colour changes from pale blue to red and is potential dependent.

Precipitation Titration

- This type of titration is very useful in determining the concentration of analyte which precipitates with the anion or titrant.
- It is useful, provided that equilibrium are rapid and a suitable means of detecting the end point is available.
- For precipitation reactions, the change in the concentration of either ion forming the precipitate may be considered.
- Consider Cl^- being titrated with AgNO_3 which is similar to acid-base titration. Prior to the equivalence point, part of the Cl^- is consumed by AgNO_3 to precipitate AgCl . The pH is determined by the remaining Cl^- in the system.
- At equivalence point, there is saturated solution with AgCl . The Cl^- is almost exactly the same with AgNO_3 added, while at points beyond the equivalence point, this is determined from the concentration of Ag^+ and K_{sp} values.
- The smaller the K_{sp} , the larger the break at equivalence point.

Indicators for silver-halide precipitation titrations

- There are two major types of indicators.
- 1. **First type** forms a coloured compound with the titrant when it is in excess. The first react specifically when an excess of titrant becomes present immediately after the end point.

Example

- Mohr's method:** if a small amount of potassium chromate is added, it will react with excess silver ions to produce deep red silver chromate in neutral solutions.
 - Volhard's method:** In acid solutions, the silver is titrated with potassium thiocyanate (KCNS) solution. Iron (III) ammonium sulfate solution is added and reacts with an excess of thiocyanate to produce a deep red iron thiocyanate species.
2. **The second type** of indicator is **adsorption indicator**. The indicator becomes adsorbed on the precipitate at the equivalence point. The colour of the indicator changes when it is adsorbed. For example, fluorescein adsorb onto the precipitate when excess silver ions are present and the precipitate takes on a pinkish color.

Complexometric titration

- Complexometric titration is a volumetric analysis where the endpoint of the analysis or titration is identified by the formation of a coloured complex.
- It is mainly useful for the determination of a mixture of different metal ions in solution.
- Complexometric titration is in the detection of mixtures of different metal ions present in the solution.
- When each drop of titrant is added, the reaction reaches an equilibrium state swiftly. There would be no chance for any interfering situations. The equivalent point can be identified very accurately using a complexometric titration.
- EDTA (ethylenediaminetetracetic acid) is used as a titrant and it is pretty much well established.

Detecting the end point in complexometric titrations

- There are methods involved when trying to detect the end point in complexometric titrations. These methods include:
 - i. the use of metal ion indicator.
 - ii. use of mercury electrode.
 - iii. Glass (pH) electrode.
 - iv. Ion -selective electrode
- However, the use of metal ion indicator appears the most convenient and efficient.

Metal Ion Indicator

- A metal-ion indicator is a compound which changes when it binds to a metal ion. It is important to note that for a metal-ion indicator to be useful, it must bind metal less strongly than EDTA does.
- There are so many different types of metal - ion indicators, which include
 - i. Erichrome Black T,
 - ii. Calmagite,
 - iii. Murexide,
 - iv. Xylenol,
 - v. Pyridylazonephthol, etc.
- Most metal ion indicators are acid-base indicators. If the metal-indicator does not dissociate easily to release metal to EDTA to form metal-EDTA complex, the metal is said to be blocked. However, the blocked EDTA can be titrated through back titration.

Self Assessment Exercise

- Highlight the general requirements for titrimetric analyses.
- Explain the following terms: (a) Blank titration (b) Basic titration (c) primary standards (d) Titration error
- Briefly explain the various classes of volumetric analysis.
- Give concise meaning of the following terms: (a) back titration, (b) standard solution, (c) equivalence point.
- Differentiate between end point and equivalence point.
- What is an (a) oxidizing agent, (b) a reducing agent? Give two examples in each case.
- Name the various types of indicators often used in Redox titration. Write briefly about each of the named indicators.

Further reading and Other resources

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