## Standard solution and Titration م.م زينب يحيى كاظم

# Standard solution and Titration 

## Titration


titrant known
concentration
analyte unknown concentration

## Volumetric Analysis - Principles Standard Solutions

- "Titrimetric" - determination of analyte by reaction with measured amount of standard reagent
- "Standard Solution" (titrant) - reagent of known concentration
- "Titration" - slow addition of titrant to analyte solution from a volumetric vessel (buret)
- "Equivalence Point" - reached when amount of added titrant is chemically equivalent to amount of analyte present in the sample.
- "End Point" - the occurrence of an observable physical change indicating that the equivalence point is reached. Might differ from Eq.Pt.!


## Standard solution

In analytical chemistry, a standard solution is a solution containing a quite known concentration of an element or a substance, a known weight of solute is dissolved to make a specific volume. It is prepared using a standard substance such as a primary standard.

## Standard solution

Standard solutions are used to determined the concentrations of other substance such as solutions in titration. The concentrations of standard solutions an normally expressed in units of moles per liter ( $\mathrm{mol} / \mathrm{L}$, often abbreviated to M for molarity), moles per cubic decimeter (mol/dm3),

## Properties

The properties of a standard solution for titrations are:

1. Its concentration must remain constant all the time. This is so that there is no need for restandardization.
2. Its reaction with the analyte must be rapid in order to minimize the waiting period after addition of each reagent.
3. Its reaction must be reasonably complete.
4. It should be possible to describe the reaction by a balanced chemical reaction.
5. A method must exist for detecting the equilibrium point.

## How to mix a Standard Solution



## Process of Making a Standard Solution from Liquids



## Volumetric Analysis - Principles Standard Solutions

- Primary Standard " -
- highly purified compound used as a reference material in titrimetry
- Properties:
- High purity
- Stable in air
- Independent of relative humidity
- Readily available
- Reasonable solubility
- Large formula weight


## Volumetric Analysis - Principles Standard Solutions

- "Secondary Standard"
- do not meet requirements for a primary standard but are available with sufficient purity and properties to be generally acceptable
- Desirable properties of a Standard Solution:
- Prepared from primary standard
- Stable
- Reacts rapidly and completely with analyte
- Reacts selectively with analyte


## Volumetric Analysis - Principles Examples of Standard Materials

- Primary
- Potassium Acid Phthalate
- $\mathrm{KHC}_{8} \mathrm{H}_{4} \mathrm{O}_{4}$ (FW 204.23)
- Benzoic Acid
- $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$ (FW 122.12)
- $\mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{KH}\left(\mathrm{IO}_{3}\right)_{2}$
- Arsenio us Oxide $\left(\mathrm{As}_{2} \mathrm{O}_{3}\right)$
- Sodium Oxalate $\left(\mathrm{Na}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right)$
- KI , $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$, Fe (pure)
- Secondary
- $\mathrm{NaOH}, \mathrm{KOH}, \mathrm{Ba}(\mathrm{OH})_{2}$
- $\mathrm{HCl}, \mathrm{HNO}_{3}, \mathrm{HClO}_{4}$
- Sulfamic Acid $\left(\mathrm{HSO}_{3} \mathrm{NH}_{2}\right)$
- $\mathrm{KMnO}_{4}, \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$
- $\mathrm{Ce}\left(\mathrm{HSO}_{4}\right)_{4}(\mathrm{FW} 632.6)$

A standard solution has known molarity.
A primary standard is made by weighing a pure solid and diluting in a volumetric flask.
A secondary standard requires a titration to calibrate its concentration. It was made using an acid or base with suspect purity.

## Not suitable <br> Arrhenius bases <br> Strong acids

Suitable
solid bronsted bases
solid weak acids

| Example | Reason |
| :--- | :--- |
| NaOH | Hydroscopic |
| HCl | volatile liquids or gases |

$\mathrm{Na}_{2} \mathrm{CO}_{3} \quad$ pure solid
$\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ pure solid

## Primary Standard

## $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4(\mathrm{~s})}$

$\mathrm{Na}_{2} \mathrm{CO}_{3(\mathrm{~s})}$
$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}_{(\mathrm{s})}$
$\mathrm{KC}_{6} \mathrm{H}_{5} \mathrm{COO}_{(\mathrm{s})}$

Secondary Standard
$\mathrm{H}_{2} \mathrm{SO}_{4(1)}$
$\mathbf{N H}_{3(\mathrm{~g})}$
$\mathrm{NaOH}_{(\mathrm{s})}$
$\mathrm{HCl}_{(\mathrm{g})}$

## Titrations

Strong Acid - Strong Base $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
pH changes slowly initially, changes rapidly through $\mathrm{pH}=7$ (equivalence point) and then changes slowly again
If the analyte is a strong acid, pH increases as base is added


## Titrations

If the analyte is a strong base, pH decreases as acid is added


## Strong Acid-Weak Base and Weak Acid - Strong Base



## Titrations

Changes in pH during a titration of a weak acid/base with a strong base/acid:
Halfway to the stoichiometric point, the $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$ of the acid

The pH is greater than 7 at the equivalence point of the titration of a weak acid and strong base
The pH is less that 7 at the equivalence point of the titration of a weak base and strong acid

Beyond the equivalence point, the excess strong acid or base will determine the pH of the solution

What was the molar concentration of 51.4 mL of a solution of $\mathrm{HNO}_{3}$ that required 29.20 mL of a 0.0160 M standard solution of KOH for complete neutralization?

Ans. It is first necessary to determine the stoichiometry of the reaction

$$
\mathrm{HNO}_{3}(\mathrm{aq})+\mathrm{KOH}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{K}^{+}(\mathrm{aq})+\mathrm{NO}_{3}^{-}(\mathrm{aq})
$$

The net ionic equation is

$$
\mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

The stoichiometry is $1 \mathrm{HNO}_{3} /{ }_{1} \mathrm{KOH}$, and therefore

$$
\begin{aligned}
& M_{\text {acid }} \times V_{\text {acid }}=M_{\text {base }} \times V_{\text {base }} \\
& M_{\text {acid }} \times 51.4 m l=29.20 m l \times 0.0160_{M} \\
& M_{\text {acid }}=0.0091_{M}
\end{aligned}
$$

## Titration Calculation

6.50 mL of $0.100 \mathrm{M} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ is required to neutralize 10.0 mL of NaOH solution in a titration. Calculate the base concentration.

| $1 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ | $+\quad 2 \mathrm{NaOH}$ | $\rightarrow \mathrm{Na}_{2} \mathrm{C}_{2} \mathrm{O}_{4}+2 \mathrm{H}_{2} \mathrm{O}$ |
| :--- | :--- | :--- |
| 0.00650 L |  |  |
| 0.100 M |  |  |
| 0.0100 L |  |  |
|  |  |  |

$0.00650 \mathrm{LH}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \times \underline{0.100 \text { mole }} \times 2 \underline{\text { mole } \mathrm{NaOH}}$
$[\mathrm{NaOH}]=1 \quad 1 \mathrm{~L} \quad 1$ mole $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$
0.0100 L

$$
=\quad 0.130 \mathrm{M}
$$

What was the molar concentration of 32.80 mL of an $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution which required 31.72 mL of a 0.0240 M standard solution of KOH for complete neutralization?

Ans. First determine the stoichiometry of the reaction

$$
\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})+2 \mathrm{KOH}(\mathrm{aq}) \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+2 \mathrm{~K}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq})
$$

The net ionic equation is

$$
2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

The stoichiometry is $1 \mathrm{H}_{2} \mathrm{SO}_{4} / 2 \mathrm{KOH}$. We must therefore take this into account in our calculations. Our formula basically tells us that in a neutralization reaction

$$
\begin{gathered}
\text { Moles acid }=\text { moles base } \\
\left(\frac{\mathrm{mol}(\text { acid })}{\mathrm{L}(\text { acid })}\right)[\mathrm{L}(\text { acid })]=\left(\frac{\mathrm{mol}(\text { base })}{\mathrm{L}(\text { base })}\right)[\mathrm{L}(\text { base })]\left(\frac{1 \text { mol }(\text { acid })}{2 \text { mol }(\text { base })}\right) \\
\left(m \mathrm{M}_{(\text {acid) }} / \mathrm{ml}\right) \times 32.80 \mathrm{ml}_{(\text {acid) }}=\left(0.0240 \mathrm{mM}_{(\text {base })} / \mathrm{ml}\right) \times 31.72 \mathrm{ml}_{(\text {base })} \times(1 / 2) \\
\left(m \mathrm{M}_{(\text {acid })} / \mathrm{ml}\right)=\mathrm{M}_{(\text {acid })}=0.0116 \mathrm{M}
\end{gathered}
$$

What was the molar concentration of 28.92 mL of an $\mathrm{H}_{3} \mathrm{PO}_{4}$ solution which required 91.21 mL of a 0.0390 M standard solution of KOH for complete neutralization?

Am. Here again, the reaction stoichiometry is central:

$$
\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})+3 \mathrm{KOH}(\mathrm{aq}) \rightleftharpoons 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+3 \mathrm{~K}^{+}(\mathrm{aq})+\mathrm{PO}_{4}^{-}(\mathrm{aq})
$$

The net ionic equation is

$$
3 \mathrm{H}^{+}(\mathrm{aq})+3 \mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons 3 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

Taking the stoichiometry, 1 mol acid $/ 3 \mathrm{~mol}$ base, into account:

$$
\begin{gathered}
\left(m \mathrm{M}_{(\text {acid })} / \mathrm{ml}\right) \times 28.92 \mathrm{ml}_{(\text {acid })}=\left(0.0390 m \mathrm{M}_{(\text {base })} / \mathrm{ml}\right) \times 91.21 \mathrm{ml}_{(\text {base })} \times(1 / 3) \\
\left(m \mathrm{M}_{(\text {acid })} / \mathrm{ml}\right)=\mathrm{M}_{(\text {acid })}=0.0410 M
\end{gathered}
$$

## Titration Error

1. Difference between endpoint and equivalence point
2. Corrected by a blank titration
3. repeat procedure without analyte
4. Determine amount of titrant needed to observe change
5. subtract blank volume from titration

## Titration



## Buffers

Buffer solutions : resists change in pH even with addition of small amounts of acid or base.

Buffer solutions are mixed solutions: mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.

Human blood has a pH maintained at $\mathrm{pH}=7.4$ due to a combination of carbonate, phosphate and protein buffers.

The ocean is buffered to a pH of $\sim 8.4$ by buffering that depends the presence of hydrogen carbonates and silicates.

## BUFFER SOLUTIONS

A buffer is a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH of a solution.
Buffers are used in all types of chemistry whenever it is desirable to maintain the pH of a solution at a constant and predetermined level

What Are the Unique Properties of Buffer Solutions?
Buffers do not maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid or base are added.

## THANK YOU

