## Fundamentals of Analytical Chemistry

م.لـ.مسـار علي عواد


## Titration and Acid-Base Neutralization



## What is Acid-Base Titration?

It is a quantitative analysis method to determine an acid's or bases' concentration by precisely neutralizing them with a standard solution of either acid or base of known concentration.

* Both titrations involve in the neutralization reaction.

$$
\mathrm{HCl}+\mathrm{KOH} \longrightarrow \mathrm{H} 2 \mathrm{O}+\mathrm{KCl}
$$

Acid + Alkali $\rightarrow$ Salt + Water

$$
\text { Or } \mathrm{H}^{+}+\mathrm{OH}^{-} \longrightarrow \mathrm{H}_{2} \mathrm{O}
$$



## What is Acid-Base Titration?

* The strength of an acid can be determined using a standard solution of a base. This process is called acidimetry.

```
HNO3 + NaOH \longrightarrow H2O + NaNO3
```

moles $\mathrm{H}_{3} \mathrm{O}^{+}=$moles $\mathrm{OH}^{-}$ $\mathbf{M} \cdot \mathbf{V} \cdot \mathbf{n}=\mathbf{M} \cdot \mathbf{V} \cdot \mathbf{n}$


## What is Acid-Base Titration?

the strength of a base can be found with the help of a standard solution of an acid, which is known as alkalimetry.


## What is Acid-Base Titration?

In general, the reaction of an acid with a base produces water and one of a class of compounds called salts.

$$
\begin{array}{ccc}
2 \mathrm{HCl}(a q) & \mathrm{Ca}(\mathrm{OH})_{2}(a q) & 1 \mathrm{~mol} \\
2 \mathrm{~mol} & \mathrm{CaCl}_{2}(a q) & +\underset{2}{2 \mathrm{H}_{2} \mathrm{O}(l)} \\
\hline 1 \mathrm{~mol} & 2 \mathrm{~mol}
\end{array}
$$

## moles $\mathrm{H}_{3} \mathrm{O}^{+}=$moles $\mathrm{OH}^{-}$ $\mathrm{M} \cdot \mathrm{V} \cdot \mathbf{2}=\mathrm{M} \cdot \mathrm{V} \cdot 1$

$$
\underset{1 \mathrm{~mol}}{\mathrm{H}_{2} \mathrm{SO}_{4}(a q)}+\underset{2 \mathrm{~mol}}{2 \mathrm{NaOH}(a q)} \longrightarrow \underset{1 \mathrm{~mol}}{\mathrm{Na}_{2} \mathrm{SO}_{4}(a q)}+\underset{2 \mathrm{~mol}}{2 \mathrm{H}_{2} \mathrm{O}(l)}
$$

## moles $\mathrm{H}_{3} \mathrm{O}^{+}=$moles $\mathrm{OH}^{-}$ $\mathrm{M} \cdot \mathrm{V} \cdot \mathbf{1}=\mathrm{M} \cdot \mathrm{V} \cdot \mathbf{2}$

## Indicators

Indicators are often added to the analyte solution to produce an observable physical change (signaling the end point) at or near the equivalence point.
$\square$ Large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance.


Indicators

Methyl Violet

Malachite green
Cresol red

Thymol blue
Benzopurpurin 4B
Orange IV
Phloxine B

2,4-Dinitrophenol

Methyl yellow (in ethanol)
Bromophenol blue
Congo red
Methyl orange
Bromocresol green
alpha-Naphthyl red

Methyl red

Litmus (azolitmin)
Bromocresol purple
4-Nitrophenol
Bromothymol blue
Phenol red

| Acid Colour | Range | Base Colour |
| :---: | :---: | :---: |
| yellow | $\begin{gathered} 0.0- \\ 1.6 \end{gathered}$ | blue |
| yellow | $0.2-$ | blue-green |
| red | $\begin{gathered} 1.0- \\ 2.0 \end{gathered}$ | yellow |
| red | $\begin{gathered} 1.2- \\ 2.8 \end{gathered}$ | yellow |
| violet | $\begin{gathered} 1.2- \\ 3.8 \end{gathered}$ | red |
| red | $\begin{gathered} 1.4- \\ 2.6 \end{gathered}$ | yellow |
| colourless | $\begin{gathered} 2.1- \\ 4.1 \end{gathered}$ | pink |
| colourless | $\begin{gathered} 2.8- \\ 4.0 \end{gathered}$ | yellow |
| red | $\begin{gathered} 2.9- \\ 4.0 \end{gathered}$ | yellow |
| yellow | $\begin{gathered} 3.0- \\ 4.6 \end{gathered}$ | blue-violet |
| blue | $\begin{gathered} 3.1- \\ 4.9 \end{gathered}$ | red |
| red | $\begin{gathered} 3.2- \\ 4.4 \end{gathered}$ | yellow |
| yellow | $\begin{gathered} 4.0- \\ 5.6 \end{gathered}$ | blue |
| red | $\begin{gathered} 4.0- \\ 5.7 \end{gathered}$ | yellow |
| red | $\begin{gathered} 4.8- \\ 6.0 \end{gathered}$ | yellow |
| red | $\begin{gathered} 5.0- \\ 7.0 \end{gathered}$ | blue |
| yellow | $\begin{gathered} 5.2- \\ 6.8 \end{gathered}$ | violet |
| colourless | $\begin{gathered} 5.4- \\ 6.6 \end{gathered}$ | yellow |
| yellow | $\begin{aligned} & 6.0- \\ & 7.6 \end{aligned}$ | blue |
| yellow | $\begin{gathered} 6.4- \\ 8.0 \end{gathered}$ | red |

## The titration of an acid with a base



Acid solution with indicator

Added base is measured with a buret.


Color change shows neutralization.

## Acid-Base Indicators

A. Finding the equivalence point of a titration

1) Use a $\mathbf{p H}$ meter
a) Plot pH versus titrant volume
b) Center vertical region = equivalence point
2) Use an Acid-Base Indicator
a) Acid-Base Indicator $=$ molecule that changes color based on $\mathbf{p H}$
b) Choose an indicator that changes color at the equivalence point
c) End Point $=$ when the indicator changes color. If you have chosen the wrong indicator, the end point will be different than the eq. pt.
d) Indicators are often Weak Acids that lose a proton (causing the color change) when [OH-] reaches a certain concentration


## Acid-base indicators

General Many indicators are weak acids and partially dissociate in aqueous solution

$$
\mathrm{HIn}_{(\mathrm{aq})} \rightleftharpoons \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{In}_{(\mathrm{aq})}^{-}
$$

The un-ionised form (HIn) is a different colour to the anionic form ( $\mathbf{I n}^{-}$).


## -increase of [H+]

- equilibrium moves to the left to give red undissociated form


## increase of $\left[\mathrm{OH}^{-}\right]$

$\mathrm{OH}^{-}$ions remove $\mathrm{H}+$ ions to form water;
$\mathrm{H}+(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})=\mathrm{H} 2 \mathrm{O}(\mathrm{l})$

- equilibrium will move to the right to produce a blue colour

Summary

$$
\mathrm{HIn}_{(\mathrm{aq})} \stackrel{\text { In acidic solution }}{\rightleftharpoons \mathrm{H}^{+}{ }_{(\mathrm{aq})}}+\mathrm{In}^{-}{ }_{(\mathrm{aq})} \quad \mathrm{pH}=\mathrm{pK}_{\text {in }} \pm 1
$$

## the behavior of an acid-type indicator

$\mathrm{HIn}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{In}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

The equilibrium-constant expression for the dissociation of an acid-type indicator takes the form

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}
$$

## Rearranging leads to

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{\mathrm{a}} \frac{[\mathrm{HIn}]}{\left[\mathrm{In}^{-}\right]}
$$

$$
\mathrm{pH}=\mathrm{pK} \mathrm{a}+\log [\mathrm{In}-] /[\mathrm{HIn}]
$$

We see then that the hydronium ion is proportional to the ratio of the concentrationof the acid form to the concentration of the base form of the indicator

The equilibrium for a base-type indicator

$$
\mathrm{In}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{InH}^{+}+\mathrm{OH}^{-}
$$



Color change and molecular modes for phenolphthalein.
(a) Acidic form after hydrolysis of the lactone form.
(b) Basic form.

## the behavior of an acid-type indicator

* we can write that the average indicator, HIn, exhibits its pure acid color when $\frac{[\mathrm{HIn}]}{\left[\mathrm{In}^{-}\right]} \geq \frac{10}{1}$
* and its base color when $\quad \frac{[\mathrm{HIn}]}{\left[\mathrm{In}^{-}\right]} \leq \frac{1}{10}$

$$
\begin{gathered}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}} \pm 1 \\
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log (1 / 10)=\mathrm{pK}_{\mathrm{a}}-\mathbf{1} \\
\mathrm{pH}=\mathrm{pKa}_{\mathrm{a}}+\log (10 / 1)=\mathrm{pK} \mathrm{a}+1
\end{gathered}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{\mathrm{a}} \frac{[\mathrm{HIn}]}{\left[\mathrm{In}^{-}\right]} \quad \longrightarrow \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10 K_{\mathrm{a}} \quad \text { or } \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.1 K_{\mathrm{a}}
$$

* Most indicators require a transition range of about 02 pH units.
* The $\mathrm{pK} a$ of the indicator should be close to the pH of the equivalence point.
* The human eye is not very sensitive to color differences in a solution containing a mixture of HIn and In . particularly when the ratio $[\mathrm{HIn}] /[\mathrm{ln} 2]$ is greater than about 10 or smaller than about 0.1. Because of this restriction.

