## Objectives

After completing this unit, the student should be able to :
1-realize the importance of the titration curves in acid - base titration .
2- Construct the various types of titration curves, their applications and requirements.
3- understand that the most important characteristics of a neutralization titration can be summarized in the titration curve .
4- Differentiate between the three important regions of the curve i.e. before, at and after the equivalent point .
5- find the values of $\mathrm{K}_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{b}}$ for weak acids and bases respectively from the titration curve .

## Introduction



Acid - base titration, which is sometimes called neutralization titration is used to titrate any species having an acidic characteristic enough $\left(\mathrm{K}_{\mathrm{a}}>1 \times 10^{-8}\right)$ where it can be titrated with a standard solution of a strong base . Like wise any species that has basic property enough $\left(\left(\mathrm{K}_{\mathrm{b}}>1 \times 10^{-8}\right)\right.$ can be titrated with a standard solution of a strong acid. The most important characteristics of a neutralization titration can be summarized in the titration curve (usually pH as a function of volume of the titrant). The titration curve can be calculated theoretically, whereupon conclusion can be drawn from it for the feasibility and the expected accuracy of a titration, and the selection of the proper indicator. The most common approach for the calculation of titration curves is based on approximations depending on the relative strength of the acid and base, the concentration levels, and the actual region of the titration curve relatively to the equivalence point.

## Titration Curves

Recall that titration is the quantitative measurement of an analyte in solution by reacting it completely with a standardized reagent. Acids and bases react until the analyte is consumed completely. A solution of base of known concentration can therefore be used to titrate an acid solution of unknown concentration. Likewise, an acid solution of known concentration can be used to titrate a base solution of unknown concentration.

This unit describes how pH changes during various acid-base titrations, therefore , before discussing the derivation of the titration curves you should go back to unit 4 and review the relevant equations of the pH calculations particularly those of strong and weak acids and bases and their salts and buffer solutions and also check out unit 3 ( stoichiometry ).

## Titration Curve

An acid - base titration curve can be derived by drawing a relationship between the pH of the titration solution ( conical flask solution ) on the $y$ - axis and the volume of the titrant ( standard solution ) which is read from the burette on the x -axis .

The importance of the titration curve lies in determining the appropriate conditions for the titration, such as the selection of the appropriate indicator and the appropriate titrant( reagent ).

## Strong Base By Strong Acid Titration Curve

## Curves for titrating strong base by strong acid :

We'll take barium hydroxide by hydrochloric acid as a typical of a strong base by a strong acid. We normally run the acid from a burette into the base in the conical flask. The following reaction is complete :

$$
2 \mathrm{HCl}+\mathrm{Ba}(\mathrm{OH})_{2} \leftrightarrow \mathrm{BaCl}_{2}+2 \mathrm{H}_{2} \mathrm{O}
$$

The following Table summarize the approximate equations that are applied for the calculations of pH before, at and after the equivalent point .

## Strong Base By Strong Acid Titration Curve

## Calculation of pH

Species in the conical
flask

Region

$$
\mathrm{pOH}=-\log 2 \mathrm{C}_{\mathrm{B}}
$$

$$
p O H=-\log \frac{2\left[\left(m L_{\mathrm{Ba(OH})_{2}} \cdot M_{\mathrm{Ba(OH})_{2}}\right)-\left(m L_{\mathrm{HCl}} \cdot M_{\mathrm{HCl}}\right)-\frac{1}{2}\right]}{m L_{\mathrm{HCL}}+m L_{\mathrm{Ba(OH})_{2}}}
$$

$$
\mathrm{Ba}(\mathrm{OH})_{2}+\mathrm{BaCl}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

Before eq. p.

$$
\mathrm{pH}=7
$$

$$
p H=-\log \frac{\left[\left(m L_{\mathrm{HCl}} \cdot M_{\mathrm{HCl}}\right)-\left(m L_{\mathrm{Ba}(\mathrm{OH})_{2}} \cdot M_{\mathrm{Ba}(\mathrm{OH})_{2}}\right) \frac{2}{1}\right]}{m L_{\mathrm{HCL}}+m L_{\mathrm{Ba}(\mathrm{OH})_{2}}}
$$

$$
\mathrm{HCl}+\mathrm{BaCl}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

## Strong Base By Strong Acid Titration Curve

Example : when 20 mL of $0.1 \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}$ was titrated with 0.2 M HCl solution, calculate the pH of the titration solution in the conical flask after the addition of the following volumes of the HCl solution ( titrant ) :
(1) omL
(2) 10 mL
(3) 20 mL
(4) 30 mL

Solution : $\mathrm{V}_{\text {eq.p. }}=[(20 \mathrm{X} 0.1) \mathrm{X} 2 / 1] / 0.2=20 \mathrm{~mL}$
(1) Before starting titration : There are only $\mathrm{Ba}(\mathrm{OH})_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ in the conical flask solution So we will calculate the pH of a strong base solution :

$$
\mathrm{pOH}=-\log 2 \mathrm{X} 0.1=0.7, \mathrm{pH}=14-0.7=13.3
$$

## Strong Base By Strong Acid Titration Curve

(2) Before equivalent point ( basic solution ) : At any point before the equivalent point ( eq.p. ), there are $\mathrm{BaCl}_{2}$ ( neutral salt ), $\mathrm{H}_{2} \mathrm{O}$ and the remaining $\mathrm{Ba}(\mathrm{OH})_{2}$ in the conical flask solution therefore the pH is calculated according to the remaining $\mathrm{Ba}(\mathrm{OH})_{2}$ thus :

$$
\begin{aligned}
& 2 \mathrm{HCl}+\mathrm{Ba}(\mathrm{OH})_{2} \rightarrow \mathrm{BaCl}_{2}+2 \mathrm{H}_{2} \mathrm{O} \\
& \text { ( I ) mmoles } 10 \mathrm{X} 0.2=2.0 \quad 20 \mathrm{X} 0.1=2.0 \quad 0 \quad 0 \\
& \begin{array}{lllll}
\text { ( C ) mmoles } & 0 & 1.0 & 1.0 & 2.0
\end{array} \\
& p O H=-\log \frac{2\left[(20 X 0.1)-\left(10 \times 0.2 X \frac{1}{2}\right)\right]}{20+10}=1.2 \quad \therefore p H=14-1.2=12.8
\end{aligned}
$$

## Strong Base By Strong Acid Titration Curve

(3) At the eq.p. ( neutral salt solution ) : There are only neutral salt $\mathrm{BaCl}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ in the conical flask solution. Therefore :

$$
\mathrm{pH}=7
$$

(4) After eq.p. ( acidic solution ): There are neutral salt $\mathrm{BaCl}_{2}, \mathrm{H}_{2} \mathrm{O}$ and the excess HCl in the conical flask solution. Therefore, the pH is calculated according to the excess HCl thus :

|  | $2 \mathrm{HCl}+\mathrm{Ba}(\mathrm{OH})_{2}$ |  |
| :--- | :---: | :---: | :---: | :---: |
| ( I ) mmoles | 30X0.2=6 | 20X0.1=2 |$\rightarrow$| $\mathrm{BaCl}_{2}+2 \mathrm{H}_{2} \mathrm{O}$ |
| :---: |
| ( C ) mmoles |
| ( 2.0 |

## Strong Base By Strong Acid Titration Curve

$p H=-\log \frac{(30 \times 0.2)-\left(20 \times 0.1 \times \frac{2}{1}\right)}{30+20}=1.4$

You can see from this example and from the graph on your right that the pH only decreases a very small amount until quite near the equivalence point, then there is a really sharp sudden decrease .


## Strong Acid By strong Base Titration Curve

Notice the effect of the concentration of the analyte $\left[\mathrm{Ba}(\mathrm{OH})_{2}\right]$ on the magnitude of the pH changes at the equivalent point region . Notice also that the pH is decreasing during titration because we are titrating a base with an acid . strong acid by strong base Titration Curve :

We'll take hydrochloric acid by sodium hydroxide as typical of a strong acid by a strong base. We normally run the base from a burette into the acid in a conical flask. The following reaction is complete:

$$
\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$



## Strong Acid By strong Base Titration Curve

This is very similar to the previous curve except, of course, that the pH starts off low and increases as you add more sodium hydroxide. Again, the pH doesn't change very much until you get close to the equivalence point. Then it surges upwards very steeply. Note the effect of the concentration of the analyte solution ( HCl ) on the magnitude of the pH changes at the equivalent point region


Example : In the case of titrating 10 mL of 0.1 M HCl by 0.2 M of NaOH , calculate the pH of the conical flask solution after the addition of the following volumes of NaOH solution :
(1) 0 mL
(2) 3 mL (3) 4.9 mL
(4) 5 mL
(5) 5.1 mL
(6) 5.2 mL ?

## Strong Acid By strong Base Titration Curve

$$
\text { Solution : } V_{\text {eq.p. }}=\frac{(10 X 0.1)}{(0.2)}=5 \mathrm{~mL}
$$

(1) : Before starting the titration, the conical flask solution contains only HCl and $\mathrm{H}_{2} \mathrm{O}$, therefore, the pH of a strong acid solution is calculated as we all know :

$$
\mathrm{pH}=-\log 0.1=1
$$

(2) : At any point before the equivalent point, the conical flask solution contains the neutral salt NaCl , $\mathrm{H}_{2} \mathrm{O}$ and the remaining HCl , therefore the pH is calculated according to the remaining HCl thus :


## Strong Acid By strong Base Titration Curve

|  | HCl | + | NaOH | $\rightarrow$ | NaCl | + |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ( I ) mmoles | $10 \mathrm{X} 0.1=1$ |  | 3X0.2=0.6 |  | 0 |  |  |  |
| ( C ) mmoles | 0.4 |  | 0 |  | 0.6 |  |  |  |

$$
p H=-\log \frac{(10 \times 0.1)-(3 \times 0.2)}{10+3}=1.5
$$

(3) : Exactly the same as (2) except using 4.9 mL instead of 3 mL of the titrant NaOH solution (i.e. just before eq.p. ) :

$$
\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$

( I ) mmoles $10 \mathrm{X} 0.1=1.0 \quad 4.9 \mathrm{X} 0.2=0.98$
$\begin{array}{lllll}(C) \text { mmoles } & 0.02 & 0 & 0.98 & 0.98\end{array}$

## Strong Acid By strong Base Titration Curve

$$
p H=-\log \frac{(10 \times 0.1)-(4.9 \times 0.2)}{10+4.9}=2.9
$$

(4) At the equivalent point . The conical flask solution contains only a neutral salt NaCl and $\mathrm{H}_{2} \mathrm{O}$ so , the solution is neutral $\mathrm{pH}=7$.
(5) : After the equivalent point, the conical flask solution contains a neutral salt ( NaCl ), $\mathrm{H}_{2} \mathrm{O}$ and the excess NaOH titrant (i.e just after eq.p. ) . Therefore, the pH is calculated as the remaining NaOH thus :

$$
\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$

( I ) mmoles $10 \mathrm{X} 0.1=1.0 \quad 5.1 \mathrm{X} 0.2=1.02$

| $(\mathrm{C})$ mmoles 0 | 0.02 | 1.0 | 1.0 |
| :--- | :--- | :--- | :--- | :--- |

## Strong Acid By strong Base Titration Curve

$$
\begin{aligned}
& p O H=-\log \frac{(5.1 \times 0.2)-(10 \times 0.1)}{10+5.1}=2.9 \\
& p H=14-2.9=11.1
\end{aligned}
$$

(6) Same as in (5) except using 5.2 mL of NaOH solution instead of 5.1 mL :

$$
\begin{aligned}
& \mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O} \\
& \text { ( I ) mmoles } 10 \mathrm{X} 0.1=1.0 \quad 5.2 \mathrm{X} 0.2=1.04 \\
& \begin{array}{lllll}
\text { ( C ) mmoles } & 0 & 0.04 & 1.0 & 1.0
\end{array} \\
& p O H=-\log \frac{(5.2 \times 0.2)-(10 \times 0.1)}{10+5.2}=2.6 \\
& p H=14-2.6=11.4
\end{aligned}
$$

## Weak Acid By Strong Base Titration Curve

You can see that the pH only rises a very small amount until quite near the equivalent point, then there is a really sharp and sudden raise. The previous graph shows the shape of the curve of this kind of titration.

Weak acid by strong base titration curve :
Let us take the titration of acetic acid by sodium hydroxide as typical example of a weak acid by a strong base
$\mathrm{NaOH}+\mathrm{CH}_{3} \mathrm{COOH} \leftrightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ Calculation of the $\mathbf{p H}$ during the titration : The following Table shows the way that pH can be
 calculated before, at and after the equivalent point .

## Weak Acid By Strong Base Titration Curve

| Calculation of pH | Species in the conical flask | Region |
| :---: | :---: | :---: |
| $p H=p K_{a}+10 \underline{\left.\frac{\left(m I_{\mathrm{NaOH}} M_{\mathrm{NaOH}}\right)}{\left(m I_{\mathrm{NaOH}}+m I_{\mathrm{CH}} \mathrm{COOH}\right.}\right)} \frac{\frac{\left.\left(\mathrm{mI} I_{\mathrm{CH}_{3} \mathrm{COOH}} M_{\mathrm{CH}_{3} \mathrm{COOH}}\right)-\left(m I_{\mathrm{NaOH}} M_{\mathrm{NaOH}}\right)\right]}{\left(m I_{\mathrm{CH}_{3} \mathrm{COOH}}+m I_{\mathrm{NaOH}}\right)}}{}$ | $\begin{gathered} \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O} \\ \text { (Buffer ) } \end{gathered}$ | Before eq.p. |
| $\text { pOF }=-10 g\| \| \frac{K_{w X}\left[\frac{\left(m I_{N a O H} \cdot M_{\text {NaOH }}\right)}{\left(m I_{N a O H}+m I_{C H 3 C O O H}\right)}\right]}{K_{a}}$ | $\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ <br> (Solution of weak acid salt) | At eq.p. |
|  | $\mathrm{NaOH}+\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ <br> ( ignore salt consider strong base only ) | After eq.p. |

## Weak Acid By Strong Base Titration Curve



Because we have got a weak acid, the beginning of the curve is obviously going to be different (gradual due to the buffer). However, once you have got an excess of base, the curve is essentially the same as before. Note that at the middle of the titration (half equivalent point ) , $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}\left([\mathrm{HA}]=\left[\left[\mathrm{A}^{-}\right]\right)\right.$so one can obtain $\mathrm{K}_{\mathrm{a}}$ of the weak acid from the curve .

## Weak Acid By Strong Base Titration Curve

At the very beginning of the curve, the pH starts by rising quite quickly as the base is added, but the curve very soon gets less steep. This is because a buffer solution is being set up - composed of the excess acetic acid and the sodium acetate being formed .
Notice that the equivalence point is now somewhat basic ( over than pH 7 ), because pure sodium acetate is a basic salt. However, the equivalence point still falls on the steepest bit of the curve. That will turn out to be


## Weak Acid By Strong Base Titration Curve

important in choosing a suitable indicator for the titration. Beyond the equivalence point (when the sodium hydroxide is in excess) the curve is just the same as that end of the HCl NaOH graph.

Example : If 10 mL of $0.1 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}\left(\left(\mathrm{K}_{\mathrm{a}}=\right.\right.$ $1.8 \times 10^{-5}$ ) is titrated with 0.2 M NaOH solution, calculate the pH of the titration solution in the conical flask after the addition of the following volumes of NaOH solution :
(1) 3 mL
(2) 5 mL
(3) 10 mL ?


## Weak Acid By Strong Base Titration Curve

Solution :

$$
V_{\text {eq. } . \mathrm{p}}=\frac{10 \times 0.1}{0.2}=5 \mathrm{~mL}
$$

(1) Before equivalent point : the remaining $\mathrm{CH}_{3} \mathrm{COOH}$ and its produced salt $\mathrm{CH}_{3} \mathrm{COONa}$ form buffer :

$$
\mathrm{NaOH}+\mathrm{CH}_{3} \mathrm{COOH} \leftrightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}
$$

( I ) mmoles $3 \mathrm{XO} 0.2=0.6 \quad 10 \mathrm{X} 0.1=1.0$
( C ) mmoles 00.4
0
0
0.6

$$
p H=-\log 1.8 \times 10^{-5}+\log \frac{(3 X 0.2) / 13}{[(10 X 0.1)-(3 X 0.2)] / 13}=4.96
$$

(2) : At equivalent point (solution of weak acid salt ) :

## Weak Acid By Strong Base Titration Curve

|  | $\mathrm{NaOH}+$ | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\leftrightarrow$ | $\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ |
| :--- | :---: | :---: | :---: | :---: |
| ( I ) mmoles | $5 \mathrm{XO} 0.2=1.0$ | $10 \mathrm{X0.1=1.0}$ | 0 | 0 |
| ( C ) mmoles | 0 | 0 | 1.0 | 1.0 |

$$
p O H=-\log \sqrt{\frac{X 10^{-14} \times[(5 \times 0.2) / 15]}{1.8 \times 10^{-5}}}=5.2 \therefore p H=14-5.2=8.8
$$

(3) : After equivalent point ( to simplify the calculation ignore salt and consider strong base only ) :

$$
\begin{array}{lcccc} 
& \mathrm{NaOH} & + & \mathrm{CH}_{3} \mathrm{COOH}
\end{array} \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}
$$

## Weak Acid By Strong Base Titration Curve

$$
\begin{aligned}
& p O H=-\log \frac{(10 X 0.2)-(10 X 0.1)}{10+10}=1.3 \\
& \therefore p H=14-1.3=12.7
\end{aligned}
$$

The graph on your right shows the effect of the strength of the acid on the shape of the titration curve. The stronger the acid the larger and the sharper the region of the curve near the equivalent point . Note that the effect of the concentration of the analyte ( weak acid ) follow the same effect previously mentioned i.e the higher the concentration the bigger and the sharper the region near the equivalent point .


Notice the effect of the strength of the acid on the curve .

## Weak Base By Strong Acid Titration Curve

## Weak base by strong acid titration curve :

This time we are going to use hydrochloric acid as the strong acid and ammonia solution as the weak base. Because you have got a weak base, the beginning of the curve is obviously going to be different (gradual due to the buffer ). However, once you have got an excess of acid, the curve is essentially the same as before.
At the very beginning of the curve, the pH starts by falling quite quickly as the acid is added, but the curve very soon gets less steep. This is because a buffer solution is being set up - composed of the excess ammonia and the ammonium chloride being formed.

## Weak Base By Strong Acid Titration Curve



Notice that the equivalence point is now somewhat acidic (less than pH 7 ), because ammonium chloride is an acidic salt .
18.4.1 Sketch the general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases, and explain their important features

## Weak Base By Strong Acid Titration Curve

However, the equivalence point still falls on the steepest bit of the curve. That will turn out to be important in choosing a suitable indicator for the titration. At the middle of titration :

$$
\left[\mathrm{NH}_{3}\right]=\left[\mathrm{NH}_{4}^{+}\right] \text {so } \mathrm{pOH}=\mathrm{pH}-14=\mathrm{pK}_{\mathrm{b}} .
$$

Calculation of the pH during the titration : The following Table shows the way that pH can be calculated, before, at and after the equivalent point :

$$
\mathrm{HCl}+\mathrm{NH}_{3} \quad \leftrightarrow \mathrm{NH}_{4} \mathrm{Cl}
$$

## VIDEO

Acid - Base Titration Curves

## Weak Base By Strong Acid Titration Curve

| pH Calculation | Species in the conical flask | Region |
| :---: | :---: | :---: |
|  | $\begin{aligned} & \mathbf{N H}_{\mathbf{3}}+\mathbf{N H}_{\mathbf{4}} \mathbf{C l} \\ & (\text { Buffer solution ) } \end{aligned}$ | Before eq.p |
| $p H=-10 \equiv \sqrt{\frac{\mathbb{K}_{w} \cdot\left[\left(m I_{\mathrm{HCl}} \cdot M_{\mathrm{HCl}} /\left(\mathrm{mL}_{\mathrm{HCl}}+m L_{\mathrm{NH}}^{3}\right)\right]\right.}{\mathbb{K}_{\mathrm{SHH}_{3}}}}$ | $\mathrm{NH}_{4} \mathrm{Cl}$ <br> (Salt of weak base) | At eq.p. |
| $p H=-\log \frac{\left(m L_{H C l} X M_{H C l}\right)-\left(m L_{N H H_{3}} X M_{N H_{3}}\right)}{m L_{H C l}+m L_{N H H_{3}}}$ | $\mathrm{HCl}+\mathrm{NH}_{4} \mathrm{Cl}$ <br> ( ignore salt consider strong acid only ) | After eq.p. |

## Weak Base By Strong Acid Titration Curve

The graph on your right shows the effect of the strength of the base on the shape of the titration curve. The stronger the base the larger and the sharper the region of the curve near the equivalent point. Note that the effect of the concentration of the analyte ( weak base ) follow the same effect previously mentioned i.e the higher the concentration the bigger and the sharper the region near equivalent point


Notice the effect of the strength of the base on the curve .

## Weak Base By Strong Acid Titration Curve

Example : If 10 mL of $0.1 \mathrm{M} \mathrm{NH}_{3}$ was titrated with 0.2 M HCl standard solution, calculate the pH of the titration solution in the conical flask after the addition of the following volumes of HCl solution : (1) 3 mL (2) 5 mL (3) 10 mL ? $\mathrm{K}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)=$ $1.75 \times 10^{-5}$

Solution : $\mathrm{V}_{\text {eq.p. }}=(10 \mathrm{X} 0.1) / 0.2=5 \mathrm{~mL}$
(1) : Before equivalent point, the remaining $\mathrm{NH}_{3}$ and the produced $\mathrm{NH}_{4} \mathrm{Cl}$ will form a buffer :

$$
\begin{aligned}
& \mathrm{HCl}+\mathrm{NH}_{3} \quad \leftrightarrow \quad \mathrm{NH}_{4} \mathrm{Cl} \\
& \text { ( I ) mmoles } 3 \mathrm{X} 0.2=0.6 \quad 10 \mathrm{X} 0.1=1.0 \quad 0 \\
& \text { ( C ) mmoles } 0 \quad 0.4 \quad 0.6
\end{aligned}
$$

## Weak Base By Strong Acid Titration Curve

$$
\begin{aligned}
p O H= & -\log 1.75 \times 10^{-5}+\log \frac{(3 \times 0.2) /(10+3)}{[(10 \times 0.1)-(3 \times 0.2)] /(10+3)} \approx 5 \\
& \therefore p H=9
\end{aligned}
$$

(2) : At the equivalent point there is only $\mathrm{NH}_{4} \mathrm{Cl}$ in the titration solution ( in the conical flask ) so we will calculate a pH of weak base salt solution :

|  | HCl | $\mathrm{NH}_{3}$ |
| :---: | :---: | :---: |
| ( I ) mmoles | 5X0.2=1.0 | 10X0.1 $=1.0$ |
| ( C ) mmoles | 0 | 0 |
| $H=-\log$ | $\frac{X 10^{-14}[5)}{1.75}$ | $\frac{2) /(10+5)]}{\left[0^{-5}\right.}=$ |


( I ) mmoles $5 \mathrm{X} 0.2=1.0 \quad 10 \mathrm{X} 0.1=1.0$ 0
$\begin{array}{llll}\text { ( }) \text { mmoles } & 0 & 0 & 1.0\end{array}$
$p H=-\log \sqrt{\frac{1 \times 10^{-14}[(5 \times 0.2) /(10+5)]}{1.75 \times 10^{-5}}}=5.2$

## Weak Base By Strong Acid Titration Curve

(3) : After the equivalent point there are $\mathrm{NH}_{4} \mathrm{Cl}$ and excess HCl in the titration solution (in the conical flask ). To simplify the calculation we will ignore $\mathrm{NH}_{4} \mathrm{Cl}$ and calculate the pH using HCl only :
$\mathrm{HCl}+\mathrm{NH}_{3} \leftrightarrow \mathrm{NH}_{4} \mathrm{Cl}$

$$
\begin{aligned}
& \text { ( I ) mmoles } 10 \mathrm{X} 0.2=2.0 \quad 10 \mathrm{X} 0.1=1.0 \quad 0 \\
& \text { ( C ) mmoles } 1.0 \quad 0 \quad 1.0 \\
& p H=-\log \frac{(10 \times 0.2)-(10 \times 0.1)}{(10+10)}=1.3
\end{aligned}
$$

Things to Remember Concerning Titration Curves:
1- In buffer region, $\mathrm{pH}=\mathrm{pKa}$. ( or $\mathrm{pK}_{\mathrm{b}}=14-\mathrm{pH}$ ) This occurs at $1 / 2$ the volume of titrant needed to reach the equivalence point.
2-The steepest region of the curve is the equivalence point.
3- The weaker the acid or the base (smaller K or large pK ), the smaller the equivalence point region.
4-The more dilute the acid or the titrant, the smaller the equivalence point region

## Weak Base By Weak Acid Titration Curve

The common example of this would be acetic acid and ammonia :

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NH}_{3(a q)} \longrightarrow \mathrm{CH}_{3} \mathrm{COONH}_{4}(\mathrm{aq})
$$

Let us consider titrating $\mathrm{NH}_{3}$ with $\mathrm{CH}_{3} \mathrm{COOH}$ This is really just a combination of graphs you have already seen. Up to the equivalent point it is similar to the ammonia - HCl case. After the equivalent point it is like the end of the acetic acid - NaOH curve ( see the graph on
 your right ).

## Weak Base By Weak Acid Titration Curve

Notice that there isn't any steep bit on this graph. Instead, there is just what is known as a "point of inflexion" because there is a buffer before equivalent point and also a buffer after it . That lack of a steep bit means that it is difficult to detect the equivalent point of a weak acid against a weak base or vice versa, therefore, the titrants in all acid - base titrations are always strong in order to get accurate and precise titration .


## Mixture Of Two Acids Or Two Bases

It is possible to titrate a mixture of two acids by a standard solution of strong base and to determine the concentration of each acid if $\mathrm{K}_{\mathrm{a} 1} \geq \mathrm{K}_{\mathrm{a} 2}$ X $10^{4}$ where $\mathrm{K}_{\mathrm{a} 1}$ is the dissociation constant of the stronger acid (acid 1 ) and $\mathrm{K}_{\mathrm{a} 2}$ is for the weaker acid (acid 2 ). In this case we will get two well defined, separated equivalent points as shown in the right graph:

If the above requirements is not met, then the two equivalent points will overlap giving one equivalent point . In this case only the total acids cab be determined. The same can be applied to the mixture of two bases ( $\mathrm{K}_{\mathrm{b} 1} \geq \mathrm{K}_{\mathrm{b} 2} \times 10^{4}$ ) as shown in the following graph :


## Curves For Weak Acid Or Weak Base Salts

Take sodium acetate as an example of weak acid salt which is basic and can be titrated with HCl ( see the right graph ) :

$$
\mathrm{HCl}+\mathrm{CH}_{3} \mathrm{COONa} \leftrightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaCl}
$$

Before the equivalent point the solution is a buffer solution . at the equivalent point it is a solution of weak acid $\mathrm{CH}_{3} \mathrm{COOH}$. After the equivalent point the solution is a mixture of HCl and $\mathrm{CH}_{3} \mathrm{COOH}$ and we will ignore the later and consider only HCl . Same thing can be repeated for weak base salt such as $\mathrm{NH}_{4} \mathrm{Cl}$ which is acidic . therefore, it can be titrated with strong base :


Notice that at midpoint $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$

## Curves For Weak Acid Or Weak Base Salts

$$
\mathrm{NaOH}+\mathrm{NH}_{4} \mathrm{Cl} \leftrightarrow \mathrm{NH}_{3}+\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$

The graph on your right shows this kind of titration where before the equivalent point there is a buffer consisting from the remaining $\mathrm{NH}_{4} \mathrm{Cl}$ and the produced $\mathrm{NH}_{3}$. At equivalent point there are neutral salt NaCl and $\mathrm{NH}_{3}$. After equivalent point we ignore $\mathrm{NH}_{3}$ and calculate the pH using only excess NaOH . Notice that at the middle of titration $\mathrm{pH}=14-\mathrm{pK}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)$.

The titration curves for the above mentioned mixtures and salts can be easily derived using the same procedures applied for the previously investigated acids and bases ( for more detail see references 1,4 and 5 ).


## Curves for polyprotic acids titration

Curves for polyproticacids titration :

Let us take the titration of $\mathrm{H}_{2} \mathrm{~A}$ by NaOH as an example :
$\mathrm{NaOH}+\mathrm{H}_{2} \mathrm{~A} \leftrightarrow \mathrm{NaHA}+\mathrm{H}_{2} \mathrm{O}\left(\mathrm{K}_{\mathrm{a} 1}\right) \quad$ (1)
$\mathrm{NaOH}+\mathrm{NaHA} \leftrightarrow \mathrm{NaA}+\mathrm{H}_{2} \mathrm{O}\left(\mathrm{K}_{\mathrm{a} 2}\right) \quad$ (2)

If $K_{a 1} \geq K_{a 2} \times 10^{4}$, then reaction (1) will complete before reaction (2) starts and we will get two well separated equivalent point as shown in the graph on your right and

Titration of $\mathrm{H}_{2} \mathrm{~A}$ with NaOH


Moles of $\mathrm{OH}^{-}$added

## Curves for polyprotic acids titration

and the curve can easily be derived as previously mentioned. If this condition is not met , then the two point will overlap giving only one point (for more details see references 1,2 and 5 ).


## Summary

In this unit , the importance of titration curves together with the theoretical calculations of the curves of all sorts of acid - base titrations have been fully investigated.
We have focused on three main regions of the curve i.e. before , at and after the equivalent point.
The way of finding $\mathrm{K}_{\mathrm{a}}$ or $\mathrm{K}_{\mathrm{b}}$ for weak acid and weak base respectively from the titration curve has been clarified .
The concepts of this units have been clarified with the help of some pictures , graphs and videos.
In the following unit ( acid - base indicators ) we will realize the important of the acid - base titration curves .

## Tutorial

Exercise 1: 10 mL of 0.1 M of analyte B is titrated with 0.2 M of titrant A according to the following equation :

$$
2 \mathrm{~A}+\mathrm{B} \leftrightarrow 3 \mathrm{D} \quad \mathrm{~K}_{\mathrm{eq}}=1 \times 10^{10}
$$

Calculate the molar concentration of each of $\mathrm{A}, \mathrm{B}$ and D after adding 5 mL of titrant solution?

Answer :

## Tutorial

Answer 1 :

$$
\begin{array}{ccccc}
2 \mathrm{~A} & +\quad \mathrm{B} & \rightarrow & 3 \mathrm{D} \\
5 \times 0.2=1.0 & 10 \times 0.1=1.0 & 0 & \text { (mmole)( } \mathrm{I}) \\
0 & 1.0-1.0 \times 1 / 2=0.5 & 1.5 & (\text { mmole })(\mathrm{C})
\end{array}
$$

The actual value of [A] can be calculated from the equilibrium constant expression thus

$$
\begin{aligned}
& 1 \times 10^{10}=\frac{(0.1)^{3}}{[A]^{2} X 0.03} \\
& {[A]=1.8 \times 10^{-6} \mathrm{M}}
\end{aligned}
$$

## Tutorial

## Exercise 2: 10 mL of 0.1 M of $\mathrm{CH}_{3} \mathrm{COOH}$ is titrated with 0.2 M NaOH . <br> Calculate the pH of the titration solution in the conical flask after the additions of 2 mL of NaOH solution ?

## Answer :

## Tutorial

Answer 2:

$$
\begin{array}{ccccc}
\mathrm{NaOH}+ & \mathrm{CH}_{3} \mathrm{COOH} \rightarrow & \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O} & \\
2 \mathrm{X0.2}=0.4 & 10 \mathrm{X} 0.1=1.0 & 0 & 0 & (\text { mmoles })(\mathrm{I}) \\
0 & 0.6 & 0.4 & 0.4 & (\text { mmoles })(\mathrm{C})
\end{array}
$$

The remaining of $\mathrm{CH}_{3} \mathrm{COOH}$ and the produced $\mathrm{CH}_{3} \mathrm{COONa}$ both form buffer solution :

$$
p H=-\log K_{a}+\log \frac{C_{s}}{C_{a}}=-\log 1.8 \times 10^{-5}+\log \frac{\frac{0.4}{2+10}}{\frac{0.6}{2+10}} \approx 4.6
$$

## Tutorial

Exercise 3 : 10 mL of 0.1 M of $\mathrm{CH}_{3} \mathrm{COOH}$ is titrated with 0.2 M NaOH . Calculate the pH of the titration solution in the conical flask after the additions of 5 mL of NaOH solution?

Answer :

## Tutorial

Answer3:

$$
\begin{array}{ccccc}
\mathrm{NaOH} \\
5 \mathrm{X} \mathrm{0.2}=1.0 & \mathrm{CH}_{3} \mathrm{COOH} \\
0 & 10 \mathrm{X} \mathrm{0.1=1.0} & \mathrm{CH}_{3} \mathrm{COONa} & +\mathrm{H}_{2} \mathrm{O} & \\
0 & 0 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
& 0 & 1.0 & 1.0 & (\text { mmole })(\mathrm{C})
\end{array}
$$

The resulting solution is a solution of the basic salt $\mathrm{CH}_{3} \mathrm{COONa}$ :

$$
\begin{aligned}
& p O H=-\log \sqrt{\frac{K_{w} X C_{s}}{K_{a}}}=-\log \sqrt{\frac{1 \times 10^{-14} \times \frac{1}{15}}{1.8 \times 10^{-5}}} \approx 5.2 \\
& \therefore p H=8.8
\end{aligned}
$$

## Tutorial

Exercise $4: 10 \mathrm{~mL}$ of 0.1 M of $\mathrm{CH}_{3} \mathrm{COOH}$ is titrated with 0.2 M NaOH . Calculate the pH of the titration solution in the conical flask after the additions of 7 mL of NaOH solution?

Answer :

## Tutorial

## Answer 4 :

$$
\begin{array}{ccccl}
\mathrm{NaOH}+ & \mathrm{CH}_{3} \mathrm{COOH} \rightarrow & \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O} & \\
7 \mathrm{X} \mathrm{0.2=1.4} & 10 \mathrm{X} 0.1=1.0 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
0.4 & 0 & 1.0 & 1.0 & (\text { mmole })(\mathrm{C})
\end{array}
$$

The resulting solution consists of NaOH ( strong base ) and $\mathrm{CH}_{3} \mathrm{COONa}$ ( basic salt ). To simplify the calculation ignore the salt and calculate the pH for a strong base solution only :

$$
p O H=-\log C_{b}=-\log \frac{0.4}{7+10}=1.6 \quad \therefore p H=12.4
$$

## ACID - BASE TITRATION CURVES

## Tutorial

Exercise 5 : 10 mL of 0.1 M of $\mathrm{CH}_{3} \mathrm{COONa}$ solution is titrated with 0.2 M HCl . Calculate the pH of the titration solution in the conical flask after the additions of 2 mL of HCl solution ?

Answer :

## Tutorial

## Answer 5 :

$$
\begin{array}{ccccc}
\mathrm{HCl}+ & \mathrm{CH}_{3} \mathrm{COONa} \rightarrow \mathrm{CH}_{3} \mathrm{COOH} & +\mathrm{H}_{2} \mathrm{O} & \\
2 \mathrm{X} 0.2=0.4 & 10 \mathrm{X} 0.1=1 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
0 & 0.6 & 0.4 & 0.4 & (\text { mmole })(\mathrm{C})
\end{array}
$$

The resulting solution composed of the remaining $\mathrm{CH}_{3} \mathrm{COONa}$ and the produced $\mathrm{CH}_{3} \mathrm{COOH}$ which is a buffer solution :

$$
p H=-\log 1.8 \times 10^{-5}+\log \frac{\frac{0.6}{2+10}}{\frac{0.4}{2+10}} \approx 4.9
$$

## Tutorial

Exercise 6: 10 mL of 0.1 M of $\mathrm{CH}_{3} \mathrm{COONa}$ solution is titrated with 0.2 M HCl . Calculate the pH of the titration solution in the conical flask after the additions of 5 mL of HCl solution?

## Answer :

## Tutorial

## Answer 6 :

$$
\begin{array}{cccccl}
\mathrm{HCl} & \mathrm{CH}_{3} \mathrm{COONa} \rightarrow \mathrm{CH}_{3} \mathrm{COOH} & +\mathrm{H}_{2} \mathrm{O} & \\
5 \mathrm{X} 0.2=1.0 & 10 \mathrm{X} 0.1=1 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
0 & 0 & 1.0 & 1.0 & (\text { mmole })(\mathrm{C})
\end{array}
$$

At the equivalent point ,the solution consists of only $\mathrm{CH}_{3} \mathrm{COOH}$ ( weak acid ) :

$$
p H=-\log \sqrt{K_{a} C_{a}}=-\log \sqrt{1.8 \times 10^{-5} \frac{1}{15}} \approx 3
$$

## Tutorial

Exercise 7 : 10 mL of 0.1 M of $\mathrm{CH}_{3} \mathrm{COONa}$ solution is titrated with 0.2 M HCl . Calculate the pH of the titration solution in the conical flask after the additions of 7 mL of HCl solution?

Answer :

## Tutorial

Answer 7 :

$$
\begin{array}{ccccr}
\mathrm{HCl}+ & \mathrm{CH}_{3} \mathrm{COONa} \rightarrow & \mathrm{CH}_{3} \mathrm{COOH} & +\mathrm{H}_{2} \mathrm{O} & \\
7 \mathrm{X} \mathrm{0.2=1.4} & 10 \mathrm{X} \mathrm{0.1}=1 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
0.4 & 0 & 1.0 & 1.0 & (\text { mmole })(\mathrm{C})
\end{array}
$$

The resulting solution consists of the excess HCl (strong acid) and the formed $\mathrm{CH}_{3} \mathrm{COOH}$ ( weak acid) so to simplify the calculation we will ignore the weak acid and calculate the pH for HCl only :

$$
p H=-\log \frac{0.4}{7+10}=1.6
$$

على الراغبين الاستماع الى محاضرات الاستاذ الاككور/ ابر اهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التلالية :

هنحنيات معاير ات الحموض و القو اعد

منحنيات معاير ات الحموض و القو اعد r

