## Acid-Base Titrations

## The Titration

- One of the most important lab procedures involving acids and bases is the titration.
- A titration is an analytical procedure that allows for the measurement of the amount of one solution that is required to exactly react with the contents of another solution.
- In acid-base terms, you add one solution to the other until the equivalence point is reached.
- The use of a pH meter will produce a pH curve (titration curve), so you can specifically calculate at what pH your solutions have been neutralized.


## Titration Types

## 1. acid-base

$\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaCl}$
2. redox
$5 \mathrm{NaC}_{2} \mathrm{O}_{4}+2 \mathrm{KMnO}_{4}+6 \mathrm{H}^{+} \rightarrow$ $10 \mathrm{CO}_{2}+2 \mathrm{Mn}^{2+}+8 \mathrm{H}_{2} \mathrm{O}$
3. precipitation
$\mathrm{Ag}^{+}+\mathrm{X}^{-} \rightarrow \mathrm{AgX}(\mathrm{s})$
4. complex formation (EDTA)
ethylenediaminetetraacetic acid


## Equivalence Point

- The point at which there are stoichiometric equivalent amounts of
- a cid and base. $\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$
- Determined by...
- indicator color change
- dramatically change in pH



## 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 ( $\mathrm{In}^{-}$).

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Apply Le Chatelier's Principle to predict any colour change
In acid - increase of [ $\mathrm{H}^{+}$]

- equilibrium moves to the left to give red undissociated form

In alkali - increase of $\left[\mathrm{OH}^{-}\right.$]

- $\mathrm{OH}^{-}$ions remove $\mathrm{H}^{+}$ions to form water; $\mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
- equilibrium will move to the right to produce a blue colour


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Summary
In acidic solution

$$
\mathrm{HIn}_{(\mathrm{aq})} \underset{\mathrm{In} \text { alkaline solution }}{\rightleftharpoons \mathrm{H}^{+}}
$$

## Acid-base indicators

Must have an easily observed colour change.
Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

## COLOUR CHANGES OF SOME COMMON INDICATORS

| pH | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| METHYL ORANGE |  |  | CHANGE |  |  |  |  |  |  |  |  |  |  |  |
| LITMUS |  |  |  |  |  | CHANGE |  |  |  |  |  |  |  |  |
| PHENOLPHTHALEIN |  |  |  |  |  |  |  | CHANGE |  |  |  |  |  |  |

## The pH range of indictors

Indictors dose not change colour sharply at one particular pH , they change over a narrow range of pH

| indctors | $\mathrm{pK}_{\text {ind }}$ | pH |
| :--- | :--- | :--- |
| litmus | 6.5 | $5-8$ |
| methylorange | 3.7 | $3.1-4.4$ |
| phenophthaline | 9.3 | $8.3-10.0$ |



## Phenolphthalein

- is a chemical compound with the formula C 20 H 14 O 4 (often written as "HIn" or "phph"). Often used in titrations, it turns colorless in acidic solutions and pink in basic solutions


Collarless acidic
Species

## Acid-base indicators

Must have an easily observed colour change. Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

To be useful, an indicator must change over the "vertical" section of the curve where there is a large change in pH for the addition of a very small volume of alkali.

The indicator used depends on the pH changes around the end point - the indicator must change during the 'vertical' portion of the curve.

In the example, the only suitable indicator is PHENOLPHTHALEIN.

## pH curves

Types There are four types of acid-base titration; each has a characteristic curve.
strong acid (HC) v. strong base ( NaOH )
weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. strong alkali $(\mathrm{NaOH})$
strong acid (HC) v. weak base $\left(\mathrm{NH}_{3}\right)$
weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. weak base $\left(\mathrm{NH}_{3}\right)$

In the following examples, alkali $(0.1 \mathrm{M})$ is added to $25 \mathrm{~cm}^{3}$ of acid $(0.1 \mathrm{M})$

End points need not be "neutral" due to the phenomenon of salt hydrolysis

## Strong Acid-Strong Base



- This diagram shows the change in pH as a solution of strong acid is slowly added to a solution of strong base.
- Strong acid-strong base titrations usually have an equivalence point around 7.
- This is due to the fact that in solution, strong acids and strong bases will both completely dissociate, so there is an approximate $1: 1$ ratio of moles of acid to moles of base at the equivalence point.


## strong acid (HC) v. strong base ( NaOH )



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## strong acid (HC) v. strong base ( NaOH )



## strong acid (HC) v. strong base ( NaOH )



## strong acid (HC) v. strong base ( NaOH )



Any of the indicators listed will be suitable - they all change in the 'vertical' portion

## strong acid (HC) v. weak base $\left(\mathrm{NH}_{3}\right)$



## strong acid (HC) v. weak base $\left(\mathrm{NH}_{3}\right)$



Only methyl orange is suitable - it is the only one to change in the 'vertical' portion

## Weak Acid-Strong Base



- At the beginning, the weak acid is in equilibrium with itself. Thus, the beginning pH is higher than that of a strong acid.
- More moles of the weak acid are required to completely react with the amount of strong base present, because the acid is not entirely dissociated.
- For every mole of base, there is less than one mole of acid able to react: there is an excess of base.
- The initial change in pH is steeper because there is excess base.
- Weak acid-strong base titrations reach their equivalence point at a pH greater than 7.


## weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. strong base $(\mathrm{NaOH})$



## weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. strong base $(\mathrm{NaOH})$



Only phenolphthalein is suitable - it is the only one to change in the 'vertical' portion

## weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. weak base $\left(\mathrm{NH}_{3}\right)$



- Weak acid-weak base titrations are difficult because each solution is in equilibrium.
- The pH of the equivalence point is around 7 .


## weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. weak base $\left(\mathrm{NH}_{3}\right)$



## Types

## weak acid $\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ v. weak base $\left(\mathrm{NH}_{3}\right)$



There is no suitable indicator- none change in the 'vertical' portion. The end point can be detected by plotting a curve using a pH meter.

## Ex. 1

What is the concentration of HCl if 30.0 mL of 0.10 M NaOH neutralizes 50.0 mL HCl ?
$\mathrm{NaOH}+\mathrm{HCl} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaCl}$
Use $\quad \mathrm{nM}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}=\mathrm{nM}_{\mathrm{b}} \mathrm{V}_{\mathrm{b}}$
$M_{a}=$

How many moles of HCl were used?
moles $=\mathrm{M}_{\mathrm{a}} \mathrm{V}_{\mathrm{a}}$, but convert the volume to $\mathrm{L}($ $50 \mathrm{~mL}=0.05 \mathrm{~L}$ ).

## Titration

- 42.5 mL of 1.3 MKOH are required to neutralize 50.0 mL of $\mathrm{H}_{2} \mathrm{SO}_{4}$. Find the molarity of $\mathrm{H}_{2} \mathrm{SO}_{4}$.
$\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{M}=$ ?
$\mathrm{V}=50.0 \mathrm{~mL} \quad \mathrm{~V}=42.5 \mathrm{~mL}$
$n=2$

$$
\begin{aligned}
& \mathrm{OH}^{-} \\
& \mathrm{M}=1.3 \mathrm{M} \\
& \mathrm{~V}=42.5 \mathrm{~mL} \\
& \mathrm{n}=1
\end{aligned}
$$

## Sample Calculation: Strong Acid-Strong Base Titration Curve

Derive the curve of the titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH .

Region 1. Before the equivalence point, after adding 20.0 mL of 0.100 M NaOH . (Half way to the equivalence point.)

Initial mmoles of $\mathrm{H}_{3} \mathrm{O}^{+}=0.100^{*} 40 \mathrm{ml}=4$ mMoles of $\mathrm{OH}^{-}$added $=0.1 * 20 \mathrm{ml}=2$

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\operatorname{amount}(\mathrm{mmol}) \text { of } \mathrm{H}_{3} \mathrm{O}^{+} \text {remaining }}{\text { original volumeof acid }+ \text { volumeof added base }}} \\
& \quad=(4-2) / 60=0.033 \\
& \mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log 0.033=1.48
\end{aligned}
$$

## Sample Calculation: Strong Acid-Strong Base Titration Curve

Region 2. At the equivalence point, after adding 40.0 mL of 0.100 M NaOH .

Initial mmoles of $\mathrm{H}_{3} \mathrm{O}^{+} 40 \mathrm{ml} \times 0.100 \mathrm{M}=4 \mathrm{mmol}_{3} \mathrm{O}^{+}$ mMoles of $\mathrm{OH}^{-}$added $40 \mathrm{ml} \times 0.100 \mathrm{M}=4 \mathrm{mmol} \mathrm{OH}^{-}$

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=\left[\mathrm{H}^{+}\right]=\sqrt{K_{w}}} \\
& \mathrm{pH}=7
\end{aligned}
$$

## Sample Calculation: Strong Acid-Strong Base Titration Curve

Region 3. After the equivalence point, after adding 50.0 mL of 0.100 M NaOH . (Now calculate excess $\mathrm{OH}^{-}$)

Total mmoles of $\mathrm{OH}^{-}=50 \mathrm{ml} \times 0.100 \mathrm{M}=5 \mathrm{mmol} \mathrm{OH}^{-}$ mMoles of $\mathrm{H}_{3} \mathrm{O}^{+}$consumed $=40 \mathrm{ml} \times 0.100 \mathrm{M}=4 \mathrm{mmol}$
$\left[\mathrm{OH}^{-}\right]=\frac{\text { amount }(\mathrm{mmol}) \text { of } \mathrm{OH}^{-} \text {remaining }}{\text { original volumeof acid }+ \text { volumeof added base }}$ $=5-4 / 90=0.011$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=1.95$
$\mathrm{pH}=14-1.95=12.05$


## Titration of strong base with strong

## acid

- In the titration of any strong base with any strong acid,

$$
\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}
$$

there are three regions of the titration curve that require different kinds of calculations:

1. Before the equivalence point, the pH is determined by excess $\mathrm{OH}^{-}$in the solution.

$$
p O H=-\log \left[O H^{-}\right]
$$

2. At the equivalence point, $\mathrm{H}^{+}$is just sufficient to react with all $\mathrm{OH}^{-}$to make $\mathrm{H}_{2} \mathrm{O}$. The pH is determined by dissociation of water.

$$
\left[\mathrm{OH}^{-}\right]=\left[\mathrm{H}^{+}\right]=\sqrt{K_{w}}
$$

3. After the equivalence point, pH is determined by excess $\mathrm{H}^{+}$in the solution.

$$
p H=-\log \left[H^{+}\right]
$$

## Calculating the pH during a weak acid-strong base titration

$$
\begin{aligned}
& \text { Initial pH } \\
& K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\left.K_{\mathrm{a}} \times[\mathrm{HA}]_{\text {init }}\right)} \\
& \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
\end{aligned}
$$

$$
\begin{aligned}
& \text { pH before equivalence point } \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{\mathrm{a}} \mathrm{x} \frac{[\mathrm{HA}]}{\left[\mathrm{A}^{-}\right]} \text {or }} \\
& \mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \left(\frac{[\text { base }]}{\text { [acid }]}\right)
\end{aligned}
$$

## Calculating the pH during a weak acid-strong base titration

## Titration of a Weak Acid by a Strong Base

Derive the curve of the titration of 25.0 mL of 0.200 M HA (acetic acid) is titrated with 0.200 M NaOH .

$$
\left(\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}\right)
$$

Determine pH in each of four regions:
(a) at the start -- before any NaOH is added

Just a simple weak acid:

$$
\left[H^{+}\right]=\sqrt{C_{H A} K_{a}}
$$

$\mathrm{pH}=2.72$
(b) before the equivalence point:
after addition of 10.0 mL of NaOH
The acid is partially neutralized by the added $\mathrm{OH}^{-}$

$$
\begin{array}{cccc}
\mathrm{HA}+\mathrm{OH}^{-} & --> & \mathrm{H}_{2} \mathrm{O}+\underset{10 \mathrm{x} 0.2}{\mathrm{~A}^{-}} \\
25 \mathrm{x} 0.2 & 10 \mathrm{x} 0.2 & & 1
\end{array}
$$

Since both HA and $\mathrm{A}^{-}$are now present, the mixture is a buffer solution!

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\mathrm{C}_{\mathrm{A}}-/ \mathrm{C}_{\mathrm{HA}}\right)
$$

[HA] left $=(25 \times 0.2-10 \times 0.2) / 35=0.085$
[ $\mathrm{A}^{-}$] produced $=(10 \times 0.2) / 35=0.057$
$\mathrm{pH}=\left(-\log 1.8 \times 10^{-5}\right)+\log (0.057 / 0.085)$
$\mathrm{pH}=4.57$
(c) at the equivalence point:

The acid (HA) is completely neutralized, and only the anion $\mathrm{A}^{-}$is present
$\therefore$ the solution is now the salt of a weak acid!
Total volume is now 50.0 mL ,

$$
\text { so }\left[\mathrm{A}^{-}\right]=0.10 \mathrm{M} \text { and } \mathrm{pH}=8.88
$$

(d) after the equivalence point:

All acid (HA) is gone and excess $\mathrm{OH}^{-}$is present
$\therefore$ the pH is determined by how much $\mathrm{OH}^{-}$is left after all the acid has been neutralized
e.g. after 40.0 mL of NaOH added: $\mathrm{pH}=12.66$


## Finding the pH During a Weak AcidStrong Base Titration

PROBLEM: Calculate the pH during the titration of 40.00 mL of 0.1000 $M$ propanoic acid (HPr; $K_{\mathrm{a}}=1.3 \times 10^{-5}$ ) after adding the following volumes of 0.1000 M NaOH :
(a) 0.00 mL (b) 30.00 mL
(c) 40.00 mL
(d) 50.00 mL

PLAN: The initial pH must be calculated using the $K_{\mathrm{a}}$ value for the weak acid. We then calculate the number of moles of HPr present initially and the number of moles of $\mathrm{OH}^{-}$added. Once we know the volume of base required to reach the equivalence point we can calculate the pH based on the species present in solution.

## SOLUTION:

(a) $\left.\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}} \times[\mathrm{HPr}]_{\text {init }}}\right)=\sqrt{\left(1.3 \times 10^{-5}\right)(0.100)}=1.1 \times 10^{-3} \mathrm{M}$
$\mathrm{pH}=-\log \left(1.1 \times 10^{-3}\right)=2.96$
(b) 30.00 mL of 0.1000 M NaOH has been added.

Initial amount of $\mathrm{HPr}=0.04000 \mathrm{~L} \times 0.1000 \mathrm{M}=4.000 \times 10^{-3} \mathrm{~mol} \mathrm{HPr}$
Amount of NaOH added $=0.03000 \mathrm{~L} \times 0.1000 \mathrm{M}=3.000 \times 10^{-3} \mathrm{~mol} \mathrm{OH}^{-}$
Each mol of $\mathrm{OH}^{-}$reacts to form 1 mol of Pr , so
Concentration (M) $\mathrm{HPr}(a q)+\mathrm{OH}^{-}(a q) \rightarrow \operatorname{Pr}(a q)+\mathrm{H}_{2} \mathrm{O}()$

| Initial | 0.004000 | 0.003000 | 0 | - |
| :--- | :---: | :---: | :---: | :---: |
| Change | -0.003000 | -0.003000 | +0.003000 | - |
| Equilibrium | 0.001000 | 0 | 0.003000 | - |

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{\mathrm{a}} \times \frac{[\mathrm{HPr}]}{[\mathrm{Pr}]}=\left(1.3 \times 10^{-5}\right) \times \frac{0.001000}{0.003000}=4.3 \times 10^{-6} \mathrm{M}
$$

$\mathrm{pH}=-\log \left(4.3 \times 10^{-6}\right)=5.37$
(c) 40.00 mL of 0.1000 M NaOH has been added.

This is the equivalence point because $\mathrm{mol}^{2} \mathrm{OH}^{-}$added $=0.004000$
$=\mathrm{mol}$ of $\mathrm{HA}_{\text {init. }}$.
All the $\mathrm{OH}^{-}$added has reacted with HA to form 0.004000 mol of $\operatorname{Pr}$.
$[\mathrm{Pr}]=\frac{0.004000 \mathrm{~mol}}{0.04000 \mathrm{~L}+0.04000 \mathrm{~L}}=0.05000 \mathrm{M}$
$\operatorname{Pr}^{-}$is a weak base, so we calculate $K_{\mathrm{b}}=\frac{K_{\mathrm{w}}}{K_{\mathrm{a}}}=\frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}}=7.7 \times 10^{-10}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \approx \frac{K_{\mathrm{w}}}{\sqrt{\left.K_{\mathrm{b}} \times\left[\mathrm{A}^{-}\right]\right)}}=\frac{1.0 \times 10^{-14}}{\sqrt{\left(7.7 \times 10^{-10}\right)(0.05000)}}=1.6 \times 10^{-9} \mathrm{M}$
$\mathrm{pH}=-\log \left(1.6 \times 10^{-9}\right)=8.80$
(d) 50.00 mL of 0.1000 M NaOH has been added.

Amount of $\mathrm{OH}^{-}$added $=0.05000 \mathrm{~L} \times 0.1000 \mathrm{M}=0.005000 \mathrm{~mol}$
Excess $\mathrm{OH}^{-}=\mathrm{OH}_{\text {added }}-\mathrm{HA}_{\text {init }}=0.005000-0.004000=0.001000 \mathrm{~mol}$
$\left[\mathrm{OH}^{-}\right]=\frac{\mathrm{mol} \mathrm{OH}_{\text {excess }}^{-}}{\text {total volume }}=\frac{0.001000 \mathrm{~mol}}{0.09000 \mathrm{~L}}=0.01111 \mathrm{M}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{\mathrm{w}}}{\left[\mathrm{OH}^{-}\right]}=\frac{1 \times 10^{-14}}{0.01111}=9.0 \times 10^{-13} \mathrm{M}$
$\mathrm{pH}=-\log \left(9.0 \times 10^{-13}\right)=12.05$

The four Major Differences Between a Strong Acid-Strong Base Titration Curve and a Weak Acid-Strong Base Titration Curve

1. The initial pH is higher.
2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point.
3. The pH at the equivalence point is greater than 7.00.
4. The steep rise interval is less pronounced.

## TITRATION CURVES

III. Weak acid with strong base

Weak base with strong acid
e.g. Titration of $\mathbf{C H}_{3} \mathbf{C O O H}$ with NaOH , Titration of $\mathrm{NH}_{4} \mathrm{OH}$ with HCl : I. At the start:


## Acid-base indicators

| Indicator | pH range | pKa | Acid Form | Base Form |
| :--- | :--- | :--- | :--- | :--- |
| methyl violet | $0.0-1.6$ | 0.8 | yellow | blue |
| thymol blue | $1.2-2.8$ | 1.6 | red | yellow |
| methyl yellow | $2.9-4.0$ | 3.3 | red | yellow |
| methyl orange | $3.1-4.4$ | 4.2 | red | yellow |
| bromocresol green $3.8-5.4$ | 4.7 | yellow | blue |  |
| methyl red | $4.2-6.2$ | 5.0 | red | yellow |
| bromothymol blue | $6.0-7.6$ | 7.1 | yellow | blue |
| phenol red | $6.4-8.0$ | 7.4 | yellow | red |
| mymol blue | $8.0-9.6$ | 9.9 | yellow | blue |
| phenolphthalein | $8.0-9.8$ | 9.9 | colourless | blue |
| thymolphthalein | $9.3-10.5$ | 11.0 | yellow | red |
| alizarin yellow $R$ | $10.1-12.0$ | 12.2 | blue | yellow |

