## pH indicators

A pH indicator is a weak acid that has different colours in the protonated and deprotonated form.


It is added in a concentration such as not to appreciably modify pH and it changes it colour according to it.

The indicator reacts in water according to this equilibrium:

$$
\begin{aligned}
& \operatorname{HInd}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \operatorname{Ind}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \\
& \qquad \mathrm{K}_{\mathrm{A}}=\frac{\left[\mathrm{Ind}^{-}\right] \cdot\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HInd}]} \quad \frac{\mathrm{K}_{\mathrm{A}}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{\left[\mathrm{Ind}^{-}\right]}{[\mathrm{HInd}]}
\end{aligned}
$$

The ratio [Ind-] / [HInd] determines the colour of the solution, we have three possible cases:

$$
\begin{array}{ll}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>\mathrm{K}_{\mathrm{A}} \rightarrow[\mathrm{HInd}]>\left[\mathrm{Ind}^{-}\right]} & \text {Red } \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{K}_{\mathrm{A}} \rightarrow[\mathrm{HInd}]=\left[\mathrm{Ind}^{-}\right]} & \text {Purple } \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]<\mathrm{K}_{\mathrm{A}} \rightarrow[\mathrm{HInd}]<\left[\mathrm{Ind}^{-}\right]} & \text {Blue }
\end{array}
$$

For a given $K_{A}$ value:

- protonated species colour ifHInd if $\mathrm{pH}<\mathrm{pK}_{\mathrm{A}}$
- ionized species colour Ind- if $\mathrm{pH}>\mathrm{pK}_{A}$
- Colour turning point if $\mathrm{pH}=\mathrm{pK}_{\mathrm{A}}$





## Rocella tinctoria tornasole



Colour variation range


Methyl orange


Bromothymol blue

fenolftalein


## Some pH indicators



## Acid-base titration

An acid-base titration is a method that allows one to determine the amount of acid (or base) present in a solution by measuring the volume of a solution of known concentration of base (or acid) needed to achieve neutralization.

The acid solution to be titrated is introduced into a container and the basic solution of known concentration is placed in a graduated burette above the container and added dropwise until the complete neutralization of the acid. From the volume of base we can calculate the number of moles of base needed to neutralize

$$
\text { moles of Base }=\text { volume } \times \text { concentration }
$$

that, for an acid monoprotic acid, coincides with the number of moles of acid. An indicator with a $\mathrm{pK}_{\mathrm{I}}=\mathrm{pK}_{\mathrm{A}}$ is also added.

## titration



A curve of acid-base titration is a plot in which it is shown the pH of a solution of acid (or base) as a function of the volume of the base (acid) added. The figure below shows the titration curve of 25 ml of 0.1 M HCl with 0.1 M NaOH


The equivalence point of a titration is the point that corresponds to the addition of a stoichiometric amount of base (or acid). For an acid-base titration of strong electrolytes the equivalence point will be at $\mathrm{pH}=7$.

Titration of a strong acid with a strong base
During the titration the pH is calculated taking into account that the number of equivalents of base added to neutralize the same number of equivalents of acid: the number of moles of acid remaining is divided by the total volume (that is increased compared to the initial value).

Initially
$\mathrm{pH}=-\log _{10} \mathrm{c}_{A}$. As the strong base $B$ is added:
$\mathrm{HA}(\mathrm{aq})+\mathrm{B}(\mathrm{aq}) \rightarrow \mathrm{BH}^{+}+\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}$ (I)

$$
\begin{aligned}
& n_{A}=c_{A} \cdot V_{\text {initial }} \\
& n_{B}=c_{B} \cdot V_{a d d e d}
\end{aligned}
$$

- when $n_{A}$ > $n_{B}$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{n_{A}-n_{B}}{V_{\text {initial }}+V_{\text {added }}}=\frac{c_{A} \cdot V_{\text {initial }}-c_{B} \cdot V_{\text {added }}}{V_{\text {initial }}+V_{\text {added }}}
$$

- when $n_{A}=n_{B} \quad \mathrm{pH}=7$ equivalence point
- then, as more base is added $n_{A}<n_{B}$

$$
\begin{equation*}
\left[O H^{-}\right]=\frac{n_{B}-n_{A}}{V_{\text {initial }}+V_{\text {added }}}=\frac{c_{B} \cdot V_{\text {added }}-c_{A} \cdot V_{\text {initial }}}{V_{\text {initial }}+V_{\text {added }}} \tag{10}
\end{equation*}
$$

$$
\mathrm{HCl}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightleftarrows \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$



## 50 ml di 0.1 M NaOH with 0.1 M HCl

$\mathrm{NaOH}(\mathrm{aq})+\mathrm{HCl}(\mathrm{aq}) \rightleftarrows \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$


Titration of a weak acid with a strong base
The titration curve has a different shape than the one for strong acids and bases. The figure below shows the titration curve of 25 ml of $0.1 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$ with 0.1 M NaOH


The titration curve of acetic acid can be divided into four parts, and for each of them a different type of calculation of pH is used.


Titration of a weak acid $\left(\mathrm{pK}_{\mathrm{A}}=4\right)$ with a strong base +pH indicator


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We will use:
Strong Acid -> H2SO4 0,01 N (0.005M\times2)
Strong Base -> NaOH 0,1 N (=0.1M)
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Calculus of equivalent $\mathrm{N} \times \mathrm{V}$, if the volume is 80 ml We will have $8 \times 10^{-4}$ eq. of acid which will be Neutralized by 8 ml of $\mathrm{NaOH} 1 \mathrm{~N}\left(0,1 \times 8 \times 10^{-3} \mathrm{I}\right)$.

We will measure the pH each time 1 ml of NaOH is added and we will draw the titration curve.
The indicator Bromothymol blue ( $\mathrm{pKa}=7$ )
will change its colour at the equivalence point.

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We will use:
Weak acid CH3}\textrm{COOH}->0,01\textrm{N}(=0.01\textrm{M}
Strong Base-> NaOH 0,1 N (=0.01M)
```

Calculus of equivalents NxV , if the vol is 80 ml we will have $8 \times 10^{-4} \mathrm{eq}$. Of acid which will be Neutralized by 8 ml di $\mathrm{NaOH} 1 \mathrm{~N}\left(0,1 \times 8 \times 10^{-3} \mathrm{I}\right)$.

We will measure the pH each time 1 ml of NaOH is added and we will draw the titration curve. The inducator Phenol red ( $\mathrm{pKa}=7.8$ ) will change its colour close to the equivalent point.

