## Weak Acid-Strong Base Titrations

## Qualitative Analysis

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\begin{gathered}
\text { weak acid }+ \text { strong base } \rightarrow \text { basic salt }+ \text { water } \\
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq})}+\mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})} \\
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq})}+\mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{Na}_{(\mathrm{aq})}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I}} \\
\mathrm{Na}^{+} \text {does not have acidic properties } \\
\text { But } \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \text { is a weak base } \\
\therefore \text { solution will be slightly basic } \\
\text { at the equivalence point. }
\end{gathered}
$$

At equivalence point,


## Quantitative Analysis

Remember, all titrations need to be analyzed in two steps:

1. As stoichiometry problems:

- How many MOLES of acid/base are in the solution? Which one is in excess, and how will that affect pH ?

2. As equilibrium problems

- In the case of weak acids or bases, what CONCENTRATION of acid/base will dissociate? This determines pH .

Example 2. $\quad \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq})}+\mathrm{NaOH}_{(\mathrm{aq})} \rightarrow \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq)}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})}$ a) Use stoichiometry to calculate the volume of NaOH that will be required to react completely with the sample of $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$.


b) Before the titrant is added, what is the pH of the solution?
© Stoichiometry: How many moles of acid are present?
(2) Consider all species in the solution. Which one controls the pH ?

No base has been added, therefore no acid has reacted yet. The solution contains the original amount of $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$.

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\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}, \quad \mathrm{H}^{+}, \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}, \quad \mathrm{H}_{2} \mathrm{O}
$$

Even though $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ is a weak acid, its $\mathrm{K}_{\mathrm{a}}$ is much higher than the $\mathrm{K}_{\mathrm{w}}$ of water $\therefore$ it controls the pH :
$\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2(\mathrm{aq}) .} \rightleftharpoons \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}{ }_{(\mathrm{aq})}$
(3) Equilibrium: What is the concentration of $\mathrm{H}^{+}$?
$\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ is a weak acid $\therefore$ it only partially dissociates.
Use the $\mathrm{K}_{\mathrm{a}}$ to find the concentration of $\mathrm{H}^{+}$at equilibrium.

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]} \stackrel{\text { sub in }}{ } 1.8 \times 10^{-5}=\frac{\left(x^{2}\right)}{(0.300-x)} \quad \begin{array}{l}
\text { 0.300/K } \\
\quad \therefore \text { use simplifying assumption }
\end{array} \\
& 1.8 \times 10^{-5} \cong \frac{\left(x^{2}\right)}{(0.300)}
\end{aligned}
$$

(4) Calculate pH

$$
\begin{aligned}
\mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right] \\
& =-\log \left(2.3 \times 10^{-3}\right) \\
\mathrm{pH} & =2.64
\end{aligned}
$$

Before any base is added, the $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ solution has a pH of $\mathbf{2 . 6 4}$.
c) At the equivalence point: After 20.0 mL of titrant is added to the sample, what is the pH ?
(1) Stoichiometry: How many moles of acid/base are present?

At the equivalence point, exactly 6.00 mmol of NaOH has been added, which reacts with the 6.00 mmol of acid initially present.
(2) Consider all species in the solution. Which one controls the pH ?

All the $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$have been consumed.

Entities in solution: $\mathrm{Na}^{+}{ }_{(\mathrm{aq})}, \quad \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$(aq), and $\mathrm{H}_{2} \mathrm{O}_{\text {(I) }}$
$\mathrm{Na}^{+}$does not affect $\mathrm{pH} \quad \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$- is a weak base and CAN affect pH . It reacts with water:

$$
\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-}
$$

To find the $K_{b}$ of this weak conjugate base,
use the $K_{a}$ of its acid:
$\mathrm{K}_{\mathrm{w}}=\mathrm{K}_{\mathrm{a}} \times \mathrm{K}_{\mathrm{b}}$
Even though the $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$is small, it is still much larger than the $\mathrm{K}_{\mathrm{w}}$ for water.
$\mathrm{K}_{\mathrm{b}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{a}}}=\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$
$\mathrm{K}_{\mathrm{b}}=5.6 \times 10^{-10}$
Therefore, the $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$will control the pH .
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(3) Equilibrium:

What is the concentration of $\mathrm{OH}^{-}$?

$\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}$
$5.6 \times 10^{-10}=\frac{\left(x^{2}\right)}{(0.150-x)} \cong \frac{\left(x^{2}\right)}{(0.150)}$
$x \cong 9.2 \times 10^{-6} \mathrm{~mol} / \mathrm{L}=\left[\mathrm{OH}^{-}\right]$
$0.150 / K_{b}>100$ $\therefore$ use simplifying assumption $x / 0.150=0.0061 \%$ $\therefore$ assumption was valid
(4) Calculate pOH and pH

$$
\begin{aligned}
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
&=-\log \left(9.2 \times 10^{-6}\right) \\
& \mathrm{pOH}=5.04 \\
& \\
& \mathrm{pH}=14.00-\mathrm{pOH} \\
&=14.00-5.04 \\
& \mathrm{pH}=8.96
\end{aligned}
$$

## Homework

- Pg. 554 \#1, 2
- Pg. 557 \#4-6, 8

A typical pH curve for a weak acid-strong base titration


