## Analytical Chemistry Lecture III by/ Dr. Ekhlas Q. J.

## BUFFER SOLUTIONS



## Buffer solutions

Definition "Solutions which resist changes in pH when small quantities of acid or alkali are added." a solution that contains a weak acid/conjugate base mixture or a weak base/conjugate acid mixture

- able to neutralize acids and bases without allowing the pH of the solution to change greatly

Acidic Buffer ( $\mathrm{pH}<7$ ) made from a weak acid (ethanoic acid) + its sodium or potassium salt (sodium ethanoate)

Alkaline Buffer ( $\mathrm{pH}>7$ ) made from a weak base (ammonia) + its chloride salt (ammonium chloride)

Uses

* Standardising pH meters
* Buffering biological systems (eg in blood)
* Maintaining the pH of shampoos


## Buffers and the Common-ion Effect

A buffer works through the common-ion effect.
Acetic acid in water dissociates slightly to produce some acetate ion:

$$
\mathrm{CH}_{3} \mathrm{COOH}(a q)+\mathrm{H}_{2} \mathrm{O}(\eta) \mathrm{CH}_{3} \mathrm{COO}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)
$$

acetic acid


If $\mathrm{CH}_{3} \mathrm{COONa}$ is added, it provides a source of $\mathrm{CH}_{3} \mathrm{COO}^{-}$ion, and the equilibrium shifts to the left. $\mathrm{CH}_{3} \mathrm{COO}$ is common to both solutions.

The addition of $\mathrm{CH}_{3} \mathrm{COO}$ reduces the \% dissociation of the acid.

## Buffers

- A buffer consisting of a mixture of the weak $\operatorname{acid}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)$ and its salt $\left(\mathrm{CH}_{3} \mathrm{COONa}^{+}\right)$, and Will undergo the following changes on the addition of acid or base:
- If the base is added $(-\mathrm{OH})$ to the solution it will be buffered by the following reaction with acetic acid:
$\mathrm{CH}_{3} \mathrm{COOH}+{ }^{-} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$
So the pH will not change significantly


## Buffers

- If acid $\left(\mathrm{H}^{+}\right)$is added, it will be buffered by another reaction, this time using the salt $\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)$:
$\mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{COOH}$
The pH will not alter significantly because the $\mathrm{CH}_{3} \mathrm{COOH}$ formed is a weak acid
- Addition of more base increases $\mathrm{A}^{-}$and decreases (HA) and this doesn't alter the pH much until [ $\left.\mathrm{A}^{-}\right] \ggg>$ [HA]

The buffering power is greatest when $\mathrm{pH}=\mathrm{pKa}$, i.e. when the acid and the salt are at the same concentration

## How a Buffer Works

The buffer components ( HA and $\mathrm{A}^{-}$) are able to consume small amounts of added $\mathrm{OH}^{-}$or $\mathrm{H}_{3} \mathrm{O}^{+}$by a shift in equilibrium position.
$\mathrm{CH}_{3} \mathrm{COOH}(a q)+\mathrm{H}_{2} \mathrm{O}($ ) $) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$
$\uparrow_{\text {Added }} \mathrm{OH}^{- \text {reacts with }}$
$\mathrm{CH}_{3} \mathrm{COOH}$, causing a shift to the right.

Added $\mathrm{H}_{3} \mathrm{O}+$ reacts with $\mathrm{CH}_{3} \mathrm{COO}^{-}$, causing a shift to the left.

The shift in equilibrium position absorbs the change in $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$, and the pH changes only slightly.

$$
\mathrm{HA}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{A}^{-}(a q)
$$

Ratio [HA]/[A$]$
does not increase very much.

Ratio [HA]/[A] does not decrease very much.

$\mathrm{H}^{+}$reacts with $\mathrm{A}^{-} \quad \mathrm{OH}^{-}$reacts with HA
Effect of added $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$on a buffered system.
in buffer solution with HA \& A:

$$
\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}} \frac{[\mathrm{HA}]}{\left[\mathrm{A}^{-}\right]}
$$

- addition of $\mathrm{H}^{+}$ neutralization:

$$
\mathrm{H}^{+}+\mathrm{A}^{-} \rightarrow \mathrm{HA}
$$

* [HA] increases slightly [ $\mathrm{A}^{-}$] decreases slightly [ $\mathrm{HA} \mathrm{A}^{\prime} /\left[\mathrm{A}^{-}\right]$increases
$\left[\mathrm{H}^{+}\right]$increases
pH decreases
* addition of $\mathrm{OH}^{-}$ neutralization:

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

* [HA] decreases slightly [ $\mathrm{A}^{-}$] increases slightly $[H A] /\left[A^{-}\right]$decreases $\left[\mathrm{H}^{+}\right]$decreases pH increases


## Buffer Action

Buffer action occurs as

- the weak acid in a buffer neutralizes base.
- the conjugate base in the buffer neutralizes acid.
- the pH of the solution is maintained.


## Alkaline buffer solutions - action

Alkaline buffer
Very similar but is based on the equilibrium surrounding a weak base; AMMONIA

$$
\begin{aligned}
& \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{NH}_{4}{ }^{+}(\mathrm{aq}) \\
& \text { relative concs. HIGH LOW LOW }
\end{aligned}
$$

but one needs;
a large conc. of $\mathrm{OH}^{-}(\mathrm{aq})$ to react with any $\mathrm{H}^{+}(\mathrm{aq})$ added a large conc of $\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})$ to react with any $\mathrm{OH}^{-}(\mathrm{aq})$ added

There is enough $\mathrm{NH}_{3}$ to act as a source of $\mathrm{OH}^{-}$but one needs to increase the concentration of ammonium ions by adding an ammonium salt.

Use AMMONIA (a weak base) + AMMONIUM CHLORIDE (one of its salts)

## Buffers

- Example: Ammonia is combined with its salt, $\mathrm{NH}_{4} \mathrm{Cl}$, in sol'n:
- If acid is added to this solution, ammonia reacts with the $\mathrm{H}^{+}$:

$$
\mathrm{NH}_{3 \text { (aq) }}+\mathrm{H}^{+}{ }_{(\mathrm{aq})} \rightarrow \mathrm{NH}_{4}^{+}{ }_{(\mathrm{aq})}
$$

- If a base is added to this solution, the $\mathrm{NH}_{4}{ }^{+}$from the dissolved salt will react with the $\mathrm{OH}^{-}$:

$$
\mathrm{NH}_{4}^{+}(\mathrm{aq})=\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{NH}_{3(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

## BUFFER SOLUTION

- When an acid is added, the conjugate base converts the excess $\mathrm{H}_{3} \mathrm{O}^{+}$ion into its acid (conjugate base removes excess $\mathrm{H}_{3} \mathrm{O}^{+}$)

$$
\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq}) \rightarrow \mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

- When a base is added, the acid converts the excess $\mathrm{OH}^{-}$ion into its conjugate base and water (acid removes excess $\mathrm{OH}^{-}$ion)

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

- These reactions go to completion (large equilibrium constants)


## pH calculations of buffer solutions

Buffer consisting of a weak acid and its salt with a strong base
$\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \longleftrightarrow \mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \quad \mathrm{K}_{\mathrm{a}}$
Henderson - Hasselbalch equation
$\mathrm{pH}=\mathrm{pKa}+\log [\mathrm{A}-] /[\mathrm{HA}]$
HA - weak acid
A- - conjugated base
Buffer consisting of a weak base and its salt with a strong acid
$\mathrm{B}+\mathrm{H}_{2} \mathrm{O} \longleftrightarrow \mathrm{BH}^{+}+\mathrm{OH}^{-}$
$\mathbf{p O H}=\mathbf{p K}_{\mathbf{b}}+\log \left[\mathrm{BH}^{+}\right] /[\mathrm{B}] \quad \mathrm{B}$ - weak base $\mathrm{BH}^{+}$- conjugated acid

## The Henderson-Hasselbalch Equation

$$
\begin{gathered}
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\Lambda)=\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \\
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right][\mathrm{A}]}{[\mathrm{HA}]} \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=K_{\mathrm{a}} \times \frac{[\mathrm{HA}]}{[\mathrm{A}]} \\
-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log K_{\mathrm{a}}-\log \left(\frac{[\mathrm{HA}]}{\left[\mathrm{A}^{-}\right]}\right) \\
\mathrm{pH}=\mathbf{p} K_{\mathrm{a}}+\log \left(\frac{[\text { base }]}{[\text { acid }]}\right)
\end{gathered}
$$

## HENDERSON-HASSELBALCH EQUATION

## In general

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\frac{\mathrm{C}_{\mathrm{b}}}{\mathrm{C}_{\mathrm{a}}}\right) \quad \text { or } \quad \mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\frac{\mathrm{n}_{\mathrm{b}}}{\mathrm{n}_{\mathrm{a}}}\right)
$$

- $\mathrm{C}_{\mathrm{a}}$ and $\mathrm{C}_{\mathrm{b}}$ are the analytical concentrations of the acid and the conjugate base, respectively
- $\mathrm{n}_{\mathrm{a}}$ and $\mathrm{n}_{\mathrm{b}}$ are the number of moles of the acid and the conjugate base, respectively
$\mathrm{C}_{\mathrm{a}}=\mathrm{n}_{\mathrm{a}} / \mathrm{V}$ and $\mathrm{C}_{\mathrm{b}}=\mathrm{n}_{\mathrm{b}} / \mathrm{V}$ (concentration ratio equals mole ratio)


## PREPARING BUFFERS

- Measure the amount of weak acid (HA) to be used [or weak base (B)]
- Calculate the amount of strong base $\left(\mathrm{OH}^{-}\right)$to be added [or strong acid $\left(\mathrm{H}^{+}\right)$]
- This makes a mixture of HA and A- which is a buffer [or B and $\mathrm{BH}^{+}$]


## Or

- Add the correct proportions of the acid and its conjugate base, then check the pH


## Question 1

A buffer solution is made by adding 0.3 mol of acetic acid and 0.3 mol of sodium acetate to enough water to make 1 L of solution. Determine the pH of the buffer solution. The $\mathrm{K}_{\mathrm{a}}$ for acetic acid is $1.8 \times 10^{-5}$

```
pH}=\mp@subsup{\textrm{pK}}{\textrm{a}}{}+\operatorname{log}[\mp@subsup{\textrm{A}}{}{-}]/[HA]\quad\mp@subsup{\textrm{A}}{}{-}=\mathrm{ sodium acetate
HA = acetic acid
pH=-log(1.8 \times 10-5})+\operatorname{log}(0.3)/(0.3
pH=4.74
Question2
Calculate the pH of the buffer solution after 0.02 moles of sodium hydroxide is added?
```

1 litre of buffer contains 0.3 moles of sodium acetate and 0.3 moles of acetic acid. Sodium hydroxide is a strong base. The acetic acid will react with the base added to try to maintain the pH . What the acid loses in concentration, the salt (sodium acetate) will gain.

## $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$

| Initial conc | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{OH}^{-}$ | $\mathrm{CH}_{3} \mathrm{COO}$ |
| :---: | :---: | :---: | :---: |
| Change | 0.3 | 0 | 0.3 |
| Equil. Conc. | $0.3-0.02$ | 0.02 | $0.3+0.02$ |

$$
\begin{aligned}
& \mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left[\mathrm{A}^{-}\right] /[\mathrm{HA}] \\
& \mathrm{pH}=-\log \left(1.8 \times 10^{-5}\right)+\log (0.32) /(0.28) \\
& \mathrm{pH}=4.74+0.058 \\
& \mathrm{pH}=4.8
\end{aligned}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$. The $\mathrm{K}_{\mathrm{a}}$ of the weak acid HA is $2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$

## Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}{ }^{-3}$. The $\mathrm{K}_{\mathrm{a}}$ of the weak acid HA is $2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$

$$
K_{a}=\frac{\left[H^{+}(a q)\right]\left[A^{-}(a q)\right]}{[H A(a q)]}
$$

Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
K_{a}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

re-arrange $\quad\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{[\mathrm{HA}(\mathrm{aq})] \times \mathrm{K}_{\mathrm{a}}}{\left[\mathrm{A}^{-}(\mathrm{aq})\right]}$

## Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

re-arrange

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{[H A(a q)] \times K_{a}}{\left[A^{-}(a q)\right]}
$$

from information given
$\left[\mathrm{A}^{-}\right]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}$
$[\mathrm{HA}]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}$

## Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
K_{a}=\frac{\left[H^{+}(a q)\right]\left[A^{-}(a q)\right]}{[H A(a q)]}
$$

re-arrange

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{[H A(a q)] \times K_{a}}{\left[A^{-}(\mathrm{aq})\right]}
$$

from information given

$$
\left[\mathrm{A}^{-}\right]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}
$$

$$
[\mathrm{HA}]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}
$$

If the $K_{a}$ of the weak acid HA is $2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{0.1 \times 2 \times 10^{-4}}{0.1}=2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\left[\mathrm{A}^{-}\right]$of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
K_{a}=\frac{\left[H^{+}(a q)\right]\left[A^{-}(a q)\right]}{[H A(a q)]}
$$

re-arrange

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\frac{[H A(\mathrm{aq})] \times K_{a}}{\left[\mathrm{~A}^{-}(\mathrm{aq})\right]}
$$

from information given

$$
\begin{aligned}
& {\left[\mathrm{A}^{-}\right]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}} \\
& {[\mathrm{HA}]=0.1 \mathrm{~mol} \mathrm{dm}^{-3}}
\end{aligned}
$$

If the $K_{a}$ of the weak acid HA is $2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\begin{aligned}
{\left[\mathrm{H}^{+}(\mathrm{aq})\right] } & =\frac{0.1 \times 2 \times 10^{-4}}{0.1}=2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3} \\
\mathrm{pH} & =-\log _{10}\left[\mathrm{H}^{+}(\mathrm{aq})\right]=3.699
\end{aligned}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of the solution formed when $500 \mathrm{~cm}^{3}$ of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ of weak acid HX is mixed with $500 \mathrm{~cm}^{3}$ of a $0.2 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of its salt $\mathrm{NaX} . \mathrm{K}_{\mathrm{a}}=4 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{X}^{-}(\mathrm{aq})\right]}{[\mathrm{HX}(\mathrm{aq})]}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of the solution formed when $500 \mathrm{~cm}^{3}$ of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ of weak acid HX is mixed with $500 \mathrm{~cm}^{3}$ of a $0.2 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of its salt $\mathrm{NaX} . \mathrm{K}_{\mathrm{a}}=4 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a}} & =\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{X}^{-}(\mathrm{aq})\right]}{[\mathrm{HX}(\mathrm{aq})]} \\
\text { re-arrange } \quad\left[\mathrm{H}^{+}(\mathrm{aq})\right] & =\frac{[\mathrm{HX}(\mathrm{aq})] \mathrm{K}_{\mathrm{a}}}{\left[\mathrm{X}^{-}(\mathrm{aq})\right]}
\end{aligned}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of the solution formed when $500 \mathrm{~cm}^{3}$ of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ of weak acid HX is mixed with $500 \mathrm{~cm}^{3}$ of a $0.2 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of its salt $\mathrm{NaX} . \mathrm{K}_{\mathrm{a}}=4 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a}} & =\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{X}^{-}(\mathrm{aq})\right]}{[\mathrm{HX}(\mathrm{aq})]} \\
\text { re-arrange } \quad\left[\mathrm{H}^{+}(\mathrm{aq})\right] & =\frac{[\mathrm{HX}(\mathrm{aq})] \mathrm{K}_{\mathrm{a}}}{\left[\mathrm{X}^{-}(\mathrm{aq})\right]}
\end{aligned}
$$

The solutions have been mixed; the volume is now $1 \mathrm{dm}^{3}$

$$
\text { therefore } \begin{aligned}
{[\mathrm{HX}] } & =0.05 \mathrm{~mol} \mathrm{dm}^{-3} \text { and } \\
{\left[\mathrm{X}^{-}\right] } & =0.10 \mathrm{~mol} \mathrm{dm}^{-3}
\end{aligned}
$$

## Calculating the pH of an acidic buffer solution

Calculate the pH of the solution formed when $500 \mathrm{~cm}^{3}$ of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ of weak acid HX is mixed with $500 \mathrm{~cm}^{3}$ of a $0.2 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of its salt $\mathrm{NaX} . \mathrm{K}_{\mathrm{a}}=4 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.

$$
\begin{aligned}
& \qquad \begin{aligned}
\mathrm{K}_{\mathrm{a}} & =\frac{\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{X}^{-}(\mathrm{aq})\right]}{[\mathrm{HX}(\mathrm{aq})]} \\
\text { re-arrange } \quad\left[\mathrm{H}^{+}(\mathrm{aq})\right] & =\frac{[\mathrm{HX}(\mathrm{aq})] \mathrm{K}_{\mathrm{a}}}{\left[\mathrm{X}^{-}(\mathrm{aq})\right]}
\end{aligned} \\
& \text { The solutions have been mixed; the volume is now } 1 \mathrm{dm}^{3} \\
& \text { therefore } \quad \begin{aligned}
{[\mathrm{HX}] } & =0.05 \mathrm{~mol} \mathrm{dm}^{-3} \text { and } \\
{\left[\mathrm{X}^{-}\right] } & =0.10 \mathrm{~mol} \mathrm{dm}^{-3}
\end{aligned} \\
& \text { Substituting } \quad \begin{aligned}
{\left[\mathrm{H}^{+}(\mathrm{aq})\right] } & =\frac{0.05 \times 4 \times 10^{-5}}{0.1}=2 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3} \\
\mathrm{pH} & =-\log _{10}\left[\mathrm{H}^{+}(\mathrm{aq})\right]=4.699
\end{aligned}
\end{aligned}
$$

## Buffer Solutions

Problem: What is the pH of a buffer that has [HOAc]
$=0.700 \mathrm{M}$ and $\left[\mathrm{OAc}^{-}\right]=0.600 \mathrm{M}$ ?
$\mathrm{HOAc}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{OAc}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

$$
\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}
$$

[HOAc]
[ $\mathrm{OAc}^{-}$]
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
equilib
$0.700-x$
$0.600+x$
x
Assuming that $\mathrm{x} \ll 0.700$ and 0.600 , we have

$$
\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right](0.600)}{0.700}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.1 \times 10^{-5} \text { and } \mathrm{pH}=4.68
$$

$$
\begin{aligned}
& p H=p K a+\log \frac{\left[A^{-}\right]}{[\mathrm{HA}]} \\
& p H=4.74+\log \frac{[0.600]}{[0.700]} \\
& p H=4.68
\end{aligned}
$$

Ex: Calculate pH change when 1.0 mL of 1.0 M HCl is added to 1.0 L acetic acid/sodium acetate buffer with $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.700 \mathrm{M}$ and $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.600 \mathrm{M}$

## $\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})} \leftrightarrow \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{CH}_{3} \mathrm{COO}_{(\mathrm{aq})}^{-}$ 0.701 M

$$
\begin{aligned}
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=k a \frac{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left(1.8 \times 10^{-5}\right) \frac{[0.701]}{[0.599]}}
\end{aligned}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.1 \times 10^{-5} \mathrm{M}
$$

$$
p H=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

$$
p H=4.67
$$

## The Henderson Hasselbalch Equation (a little short cut)

- Ex: Calculate pH change when 1.0 mL of 1.0 M HCl is added to 1.0 L acetic acid/sodium acetate buffer with $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=$ 0.700 M and $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=0.600 \mathrm{M}$
- As before, after the buffer has neutralized the added HCl , the $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ in the buffer will be 0.701 M and the $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$in the buffer will be 0.599 M .

$$
\begin{aligned}
& p H=p K a+\log \frac{\left[A^{-}\right]}{[\mathrm{HA}]} \\
& p H=4.74+\log \frac{[0.599]}{[0.701]} \\
& p H=4.67
\end{aligned}
$$

Calculate the pH of a buffer solution that is 0.040 M $\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})$ and $0.080 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$. $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right)=4.75$
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \Leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$

| Initial | 0.080 M | 0 | 0.040 M |
| :--- | :---: | :--- | :--- |
| Change | -x | x | $0.040+\mathrm{x}$ |
| Equilibrium | $0.080-\mathrm{x}$ | x | $0.040+\mathrm{x}$ |

$\mathrm{K}_{\mathrm{a}}=(0.040+\mathrm{x}) \mathrm{x} /(0.080-\mathrm{x})$
Assume $x$ << 0.040

$$
\begin{aligned}
& \mathrm{x}=3.6 \times 10^{-5} \\
& \mathrm{pH}=4.44
\end{aligned}
$$

$$
\begin{aligned}
& p H=p K a+\log \frac{\left[A^{-}\right]}{[\mathrm{HA}]} \\
& p H=4.75+\log \frac{[0.040]}{[0.080]} \\
& p H=4.44
\end{aligned}
$$

## The Common Ion Effect

QUESTION: What is the effect on the pH of adding $\mathrm{NH}_{4} \mathrm{Cl}$ to $0.25 \mathrm{M} \mathrm{NH}_{3}(\mathrm{aq})$ ?
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
Let us first calculate the pH of a 0.25 M $\mathrm{NH}_{3}$ solution.

|  | $\left[\mathrm{NH}_{3}\right]$ | $\left[\mathrm{NH}_{4}{ }^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| :--- | :--- | :---: | :---: |
| initial | 0.25 | 0 | 0 |
| change | -x | +x | +x |
| equilib | $0.25-\mathrm{x}$ | x | x |

## The Common Ion Effect

QUESTION: What is the effect on the pH of adding $\mathrm{NH}_{4} \mathrm{Cl}$ to $0.25 \mathrm{M} \mathrm{NH}_{3}(\mathrm{aq})$ ?
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \quad \rightleftarrows \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

$$
\mathrm{K}_{\mathrm{b}}=1.8 \times 10^{-5}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}=\frac{\mathrm{x}^{2}}{0.25-\mathrm{x}}
$$

Assuming x is $\ll 0.25$, we have

$$
\left[\mathrm{OH}^{-}\right]=\mathrm{x}=\left[\mathrm{K}_{\mathrm{b}}(0.25)\right]^{1 / 2}=0.0021 \mathrm{M}
$$

This gives $\mathrm{pOH}=2.67$ and so - -

$$
\mathrm{pH}=14.00-2.67=11.33 \text { for } 0.25 \mathrm{M} \mathrm{NH}_{3}
$$

What is the pH of a buffer that is 0.12 M in lactic acid, $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}$, and $0.10 M$ in sodium lactate? $K_{a}$ for lactic acid is $1.4 \times 10^{-4}$.

$$
\begin{aligned}
\mathrm{pH} & =\mathrm{p} K_{a}+\log \frac{[\text { base }]}{[\text { acid }]} \\
\mathrm{pH} & =-\log \left(1.4 \times 10^{-4}\right)+\log \frac{(0.10)}{(0.12)} \\
\mathrm{pH} & =3.85+(-0.08)
\end{aligned}
$$

$$
\mathrm{pH}=3.77
$$

Suppose you want to make a pH 5.00 buffer---using acetic acid (HA) and sodium acetate ( $\mathrm{A}^{-}$)
$\mathrm{pK}_{\mathrm{a}}$ of acetic acid $=4.76$;

What ratio of HA and A should be used?
$5.00=4.76+\log \mathrm{x} ; \quad$ where $\mathrm{x}=\left(\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]\right)$
$0.24=\log x$
$10^{0.24}=x=1.74=$ ratio of moles conjugate base to acid in solution

Example :-Calculate the pH of a buffer prepared by adding 10 mL of 0.1 M acetic acid to 20 mL of 0.1 M sodium acetate ?

$$
\begin{gathered}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{[\mathrm{salt}]}{\text { acid }]} \\
\mathrm{pH}=-\log 1.75 \times 10^{-5}+\log \frac{\frac{0.1 \times 20}{\frac{30}{0.1 \times 10}}}{30} \\
\mathrm{pH}=4.76+\log 2.0=5.06
\end{gathered}
$$

We can use millimoles of acids and salt in place of molarity.

Calculate the volume of concentrated ammonia and the weight of ammonium chloride you would have take to prepare 100 mL of a buffer at pH 10.0 if the final concentration of salt is to be 0.2 M ? Where, density of ammonia $=0.9 \mathrm{~g} / \mathrm{cm}^{3}$ and percentage $=28 \%$.
$\mathrm{pOH}=\mathrm{pKb}+\log [$ salt $] /[$ base $] \quad \mathrm{pH}+\mathrm{POH}=14$
$10+\mathrm{POH}=14$
$4=4.76+\log 0.2[\mathrm{NH} 3]$
$4=4.76+\log 0.2 /[\mathrm{NH} 3]$
$-0.76=\log 0.2 /[\mathrm{NH} 3]$

$$
\mathrm{POH}=14-10=4
$$

$-0.76=\log 0.2 /[\mathrm{NH} 3]$

$$
\begin{gathered}
10^{-0.76}=\frac{0.2}{\left[\mathrm{NH}_{3}\right]} \\
{\left[\mathrm{NH}_{3}\right]=\frac{0.2}{10^{-0.76}}=\frac{0.2}{0.173}=1.15 \mathrm{M}} \\
\mathrm{M}_{1} \mathrm{~V}_{1}=\mathrm{M}_{2} \mathrm{~V}_{2} \\
\left(\frac{0.28 \times 0.9 \times 1000}{17}\right) \times \mathrm{V}_{1}=1.15 \times 10 \mathrm{O} \\
14.8 \times \mathrm{V}_{1}=1.15 \times 100 \quad, \quad \mathrm{~V}_{1}=7.8 \mathrm{~mL} \\
\mathrm{M}_{\mathrm{NH}_{4} \mathrm{Cl}}=\frac{\mathrm{wt}}{\mathrm{M} . \mathrm{wt}} \times \frac{1000}{\mathrm{VmL}} \\
0.2=\frac{\mathrm{wt}}{53.5} \times \frac{1000}{100} \quad \mathrm{wt}=1.07 \mathrm{gm} \mathrm{NH}
\end{gathered}
$$

## Example: A buffer is prepared from 60.0 mL of $0.100 \mathrm{M} \mathrm{NH}_{3}$

 and 40.0 mL of $0.100 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$. What is the pH of the buffer solution? $K_{b}=1.8 \times 10^{-5}$ for $\mathrm{NH}_{3}$.Answer: The buffer involves the $\mathrm{NH}_{3} / \mathrm{NH}_{4}{ }^{+}$conjugate acid/base pair.

$$
\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

Conc's: Since two solutions are mixed, both have been diluted.
Use this: $\mathrm{V}_{\mathrm{f}}=60.0 \mathrm{~mL}+40.0 \mathrm{~mL}=100.0 \mathrm{~mL}$
$\left[\mathrm{NH}_{3}\right]_{\mathrm{f}}=\mathrm{V}_{\mathrm{i}} \mathrm{M}_{\mathrm{i}} / \mathrm{V}_{\mathrm{f}}=(60.0 \mathrm{~mL})(0.100 \mathrm{M}) / 100.0 \mathrm{~mL}=0.0600 \mathrm{M}$
$\left[\mathrm{NH}_{4}{ }^{+}\right]_{\mathrm{f}}=\mathrm{V}_{\mathrm{i}} \mathrm{M}_{\mathrm{i}} / \mathrm{V}_{\mathrm{f}}=(40.0 \mathrm{~mL})(0.100 \mathrm{M}) / 100.0 \mathrm{~mL}=0.0400 \mathrm{M}$
Now, we can calculate pH:
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
$\begin{array}{lllc}\text { [init] } & 0.0600 & 0.0400 & 0 \\ \text { [change] } & -x & +x & +x \\ \text { [equil] } & (0.0600-x) & (0.0400+x) & x\end{array}$
$\mathrm{K}_{\mathrm{b}}=1.8 \times 10^{-5}=\frac{x(0.0400+x)}{(0.0600-x)} \approx \frac{0.0400 \mathrm{x}}{0.0600} \quad \therefore \quad \mathrm{pH}=2.7 \times 10^{-5} \mathrm{M}$
$\therefore \mathrm{POH}=-\log \left(2.7 \times 10^{-5}\right)=4.57 \quad \therefore \quad \mathrm{pH}=9.43$

If the $\mathrm{K}_{\mathrm{a}}$ of an acid is $1.0 \times 10^{-6}, \mathrm{pH}=3.00$, and the concentration of the unionized acid is $1.0 \times 10^{-2} \mathrm{M}$, what is the concentration of the salt?

## Solution

Given: $\mathrm{pH}=3.00, \mathrm{~K}_{\mathrm{a}}=1.0 \times 10^{-6} \mathrm{M}$, and $[\mathrm{HA}]=1.0 \times 10^{-2} \mathrm{M}$
solve for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-3}=1.0 \times 10^{-3} \mathrm{M}$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3}-\frac{\left.\mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}\right.}{\text { and }}
$$

rearrange equation to solve for the salt [ $\mathrm{A}^{-}$]

$$
\left[\mathrm{A}^{-}\right]=\mathrm{K}_{\mathrm{a}} \frac{[\mathrm{HA}]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=1.0 \times 10^{-6} \mathrm{M} \frac{\left[1.0 \times 10^{-2} \mathrm{M}\right]}{\left[1.0 \times 10^{-3} \mathrm{M}\right]}
$$

$$
\left[\mathrm{A}^{-}\right]=1.0 \times 10^{-5} \mathrm{M}
$$

(1)1 (a) The $\mathrm{pK}_{\mathrm{a}}$ of HF is 3.17 . Calculate the pH of a $1.00-\mathrm{L}$ solution that is 1.00 M HF and 1.50 M NaF .
(b) What is the pH of this solution after addition of 50.0 mL of 10.0 M HCl ?
Answer: (a) $\mathrm{pH}=3.35$
(b) $\mathrm{pH}=2.99$

Q2;Calculate the pH of a solution prepared by adding 25 mL of 0.1 M sodium hydroxide to 30 mL of 0.2 M acetic acid?

- A 1.0 L buffer solution contains $0.50 \mathrm{M} \mathrm{NH} 3(\mathrm{pKb}=4.75)$ and 0.20 M NH 4 Cl . Calculate the pH upon addition of 0.010 mol of solid NaOH .

