## 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 $\mathrm{H}^{+}$:

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

- 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
$\mathrm{B}+\mathrm{H}_{2} \mathrm{O} \longleftrightarrow \mathrm{BH}^{+}+\mathrm{OH}^{-}$
$\mathbf{p O H}=\mathbf{p K}_{\mathrm{b}}+\log \left[\mathrm{BH}^{+}\right] /[\mathrm{B}] \quad \mathrm{B}$ - weak base $\mathrm{BH}^{+}$- conjugated acid

## The Henderson-Hasselbalch Equation

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

## HENDERSON-HASSELBALCH EQUATION

In general
$\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\frac{\mathrm{C}_{\mathrm{b}}}{\mathrm{C}_{\mathrm{a}}}\right) \quad$ 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 $\mathrm{A}^{-}$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 $1.8 \times 10^{-5}$

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left[\mathrm{A}^{-}\right] /[\mathrm{HA}] \quad \mathrm{A}^{-}=\text {sodium acetate }
$$

$$
\mathrm{HA}=\text { acetic acid }
$$

$\mathrm{pH}=-\log \left(1.8 \times 10^{-5}\right)+\log (0.3) /(0.3)$
$\mathrm{pH}=4.74$
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.

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

|  | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{OH}^{-}$ | $\mathrm{CH}_{3} \mathrm{COO}$ |
| :---: | :---: | :---: | :---: |
| Initial conc | 0.3 | 0 | 0.3 |
| Change | $0.3-0.02$ | 0.02 | $0.3+0.02$ |
| Equil. Conc. | 0.28 | 0.02 | 0.32 |

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

## 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 $2 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$

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

