## Buffers

How can a solution neutralize both acids and bases?

## Why?

Buffer solutions are a mixture of substances that have a fairly constant pH regardless of addition of acid or base. They are used in medicine, industry and manufacturing to keep the pH of a solution stable regardless of other reactions that might be occurring. You have buffers in your blood, for example, because the proper function of enzymes is dependent on the pH of your blood staying in a narrow range. Eating, breathing and exercising can all alter the acidity or basicity of your blood, but the buffers in your blood help control the pH and keep all of your enzymes working properly.

## Model 1 - Comparing Solutions:

Beaker A: 100 mL Pure Water

| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$ |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
| WB $\quad$ WA |  | CA |  | CB |

Beaker B: 100 mL of 1.00 M HCl
$\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$

| SA |  | WB |  | CA |
| :---: | :---: | :--- | :---: | :---: |
|  | $\mathbf{H C l}$ | $\rightarrow$ | $\mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}$ | $\mathbf{C l}^{-}$ |
| $\mathbf{I}$ | 1.00 |  | 0 | 0 |
| $\mathbf{C}$ | -1.00 |  | +1.00 | +1.00 |
| $\mathbf{F}$ | 0 |  | 1.00 | 1.00 |

Beaker D: 100 mL of $1.00 \mathrm{M} \mathrm{HNO}_{2}$ mixed with 100 mL of $1.00 \mathrm{M} \mathrm{NaNO}_{2}$ (Be careful-dilution!!!)

|  | $\mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{2}^{-}(\mathrm{aq})$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | WA | WB | CA | CB |
|  | $\mathrm{HNO}_{2}$ | $\rightleftharpoons$ | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{NO}_{2}{ }^{-}$ |
| I | 0.500 |  | 0 | 0.500 |
| C | -x |  | +x | +x |
| E | $0.500-\mathrm{x}$ |  | x | $0.500+\mathrm{x}$ |
|  | 0.500 |  | $4.6 \times 10^{-4}$ | 0.500 |

$K_{a}=4.6 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}=\frac{x \cdot x}{1.00-x}$
$4.6 \times 10^{-4} \approx \frac{x^{2}}{1.00}$ and $x=2.1 \times 10^{-2}$
$K_{a}=4.6 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}=\frac{x(0.500+x)}{(0.500-x)}$
$4.6 \times 10^{-4} \approx \frac{x(0.500)}{0.500}$ and $x=4.6 \times 10^{-4}$

1. For each beaker in Model 1, underneath each reaction equation, write SA (strong acid), SB (strong base), WA (weak acid), or WB (weak base) for the reactants; and write CA (conjugate acid) or CB (conjugate base) for the products.
2. For Beaker A and B, fill in the ICE/ICF charts to determine all equilibrium/final concentrations of the molecules or ions. ICF ("final") is used for reactions that go to completion, such as reactions with strong acids or bases. For these the change will stoichiometrically consume the limiting reactant.
3. For Beaker C and D, fill in the ICE charts, using " $x$ " values as needed. Then, underneath each ICE chart, write the $\mathrm{K}_{\mathrm{a}}$ expression and show calculations to determine the value of " $x$." Then, go back and modify values in the Equilibrium row so that each concentration is a numerical value. (Substitute in all " $x$ " values.)
4. Imagine that 1.00 M sodium hydroxide was added dropwise to each of the beakers in Model 1. List the species in each beaker that would react with this added base and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write "none."

| Beaker A <br> Pure Water | Beaker B <br> $\mathrm{HCl}(\mathrm{aq})$ | Beaker C <br> $\mathrm{HNO}_{2}(\mathrm{aq})$ | Beaker D <br> $\mathrm{HNO}_{2}$ with $\mathrm{NaNO}_{2}$ |
| :---: | :---: | :---: | :---: |
| none | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{HNO}_{2}$ | $\mathrm{HNO}_{2}$ |

5. Imagine that 1.00 M hydrochloric acid was added dropwise to each of the beakers in Model 1. List the species in each beaker that could react with this added acid and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write "none."

| Beaker A <br> Pure Water | Beaker B <br> $\mathrm{HCl}(\mathrm{aq})$ | Beaker C <br> $\mathrm{HNO}_{2}(\mathrm{aq})$ | Beaker D <br> $\mathrm{HNO}_{2}$ with $\mathrm{NaNO}_{2}$ |
| :---: | :---: | :---: | :---: |
| none | none | none | $\mathrm{NO}_{2}^{-}$ |

6. Which beaker in Model 1 was able to neutralize significant quantities of both acid and base? D

## Read This!

A buffer solution is one that can neutralize both small quantities of acid and small quantities of base. This is possible because the solution contains significant quantities of both a weak acid and a weak base (the weak base is usually the conjugate base of the weak acid). Thus, a buffer can neutralize a significant amount of any strong acid or any strong base that is added, allowing the solution to keep a fairly constant pH .
7. Which beaker in Model 1 contains a buffer? D For this buffer...
a) What species is the weak acid? $\mathrm{HNO}_{2}$ $\qquad$ What species is the weak base? $\mathrm{NO}_{2}^{-}$
b) Write the neutralization reaction that would take place if 1.0 M NaOH was added to this buffer. (Hint-what species in the buffer will react with the added $\mathrm{OH}^{-}$?) Also, explain why the pH of the solution would stay fairly constant after the addition of some NaOH .

$$
\mathrm{NaOH}(\mathrm{aq})+\mathrm{HNO}_{2}(\mathrm{aq}) \rightarrow \mathrm{NaNO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

$$
\text { Net Ionic: } \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HNO}_{2}(\mathrm{aq}) \rightarrow \mathrm{NO}_{2}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

The pH stays fairly constant because the weak acid $\left(\mathrm{HNO}_{2}\right)$ in the buffer consumes all of the added strong base $\mathrm{OH}^{-}$and forms the weak base $\mathrm{NO}_{2}{ }^{-}$and water. Thus, all strong base has been removed and for small amounts of $\mathrm{OH}^{-}$, the relative amounts of $\mathrm{HNO}_{2}$ and $\mathrm{NO}_{2}^{-}$remain fairly constant. Thus, the $\left[\mathrm{H}^{+}\right]$, as calculated for beaker D above, remains fairly constant.
c) Write the neutralization reaction that would take place if 1.0 M HCl was added to this buffer. (Hintwhat species in the buffer will react with the added $\mathrm{H}_{3} \mathrm{O}^{+}$?) Also, explain why the pH of the solution would stay fairly constant after the addition of some HCl .

$$
\begin{gathered}
\mathrm{HCl}(\mathrm{aq})+\mathrm{NaNO}_{2}(\mathrm{aq}) \rightarrow \mathrm{HNO}_{2}(\mathrm{aq})+\mathrm{NaCl}(\mathrm{aq}) \\
\text { Net Ionic: } \mathrm{H}^{+}(\mathrm{aq})+\mathrm{NO}_{2}^{-}(\mathrm{aq}) \rightarrow \mathrm{HNO}_{2}
\end{gathered}
$$

As above, the pH stays fairly constant because the weak base $\left(\mathrm{NO}_{2}^{-}\right)$in the buffer consumes all the added strong acid $\mathrm{H}^{+}$and forms the weak acid $\mathrm{HNO}_{2}$ and water. Thus, all strong acid has been removed and for small amounts of $\mathrm{H}^{+}$, the relative amounts of $\mathrm{HNO}_{2}$ and $\mathrm{NO}_{2}^{-}$remain fairly constant. Thus, the $\left[\mathrm{H}^{+}\right]$, as calculated for beaker D above, remains close to the $\mathrm{K}_{\mathrm{a}}$.

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d) Now suppose one keeps adding 1.0 M HCl to this buffer until a total of 101 mL of 1.0 M HCl have been added. At this point, the pH of the solution will be very acidic. Why is this the case?

At this point, 0.101 mol of HCl will have been added to 0.100 mol of $\mathrm{NO}_{2}^{-}$, completely using it up and leaving behind an excess of 0.001 mol of $\mathrm{H}^{+}$in 301 mL , for a concentration of 0.0033 M and a pH of 2.479.
8. Fill in the chart below to determine which of the following solutions are buffer solutions. To do so, first, determine the three most predominant species in the solution. Second, underneath each predominant species, label each with either strong acid (SA), strong base (SB), weak acid (WA), weak base (WB) or neutral ion (N) (A neutral ion could be a the conjugate base of a strong acid and so would be too weak to be a base in $\mathrm{H}_{2} \mathrm{O}$, or it could be the conjugate acid of a strong base and so would be too weak to be an acid in $\mathrm{H}_{2} \mathrm{O}$ ). Lastly, state whether the solution is a buffer solution.

| Substances mixed in equal volumes | List the three most predominant species in the solution. Underneath each species, label with either SA, SB, WA, WB or $\mathbf{N}$ |  |  | Is the solution a buffer? |
| :---: | :---: | :---: | :---: | :---: |
| a) 1.0 M HCl and 1.0 M NaCl | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{Na}^{+}$ | No |
|  | SA | N | N |  |
| b) $1.0 \mathrm{M} \mathrm{HNO}_{2}$ and $1.0 \mathrm{M} \mathrm{HNO}_{3}$ | $\mathrm{HNO}_{2}$ | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{NO}_{3}{ }^{-}$ | No |
|  | WA | SA | N |  |
| c) $1.0 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ and $1.0 \mathrm{M} \mathrm{NH}_{3}$ | $\mathrm{NH}_{4}^{+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{NH}_{3}$ | Yes |
|  | WA | N | WB |  |
| d) $1.0 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$ and 1.0 M NaCl | $\mathrm{CH}_{3} \underline{\mathrm{COOH}}$ | $\mathrm{Na}^{+}$ | $\mathrm{Cl}^{-}$ | No |
|  | WA | N | N |  |
| e) 1.0 M HF and 1.0 M NaF | HF | $\mathrm{Na}^{+}$ | $\mathrm{F}^{-}$ | Yes |
|  | WA | N | WB |  |
| f) $1.0 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ and $1.0 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$ | $\mathrm{Na}^{+}$ | $\mathrm{HSO}_{4}{ }^{-}$ | - | No |
|  | N | WA |  |  |
| g) 1.0 M KOH and 1.0 M KCl | $\mathrm{K}^{+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{OH}^{-}$ | No |
|  | N | N | SB |  |
| h) $1.0 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$ and 1.0 M HCl | $\mathrm{Ca}^{2+}$ | $\mathrm{Cl}^{-}$ | $\mathrm{OH}^{-}$ | No |
|  | N | N | SB |  |

## Model 2 - pH of Buffer Solutions

## Beaker 1

$100 \mathrm{~mL} 1.0 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ and $100 \mathrm{~mL} 1.0 \mathrm{M} \mathrm{NH}_{3}$
$\mathbf{N H}_{4}{ }^{+}(\mathrm{aq})+\mathbf{H}_{2} \mathbf{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathbf{N H}_{3}(\mathrm{aq})$
$K_{\mathrm{a}}$ of $\mathrm{NH}_{4}^{+}=5.6 \times 10^{-10} \quad \mathrm{pK}_{\mathrm{a}}$ of $\mathrm{NH}_{4}^{+}=9.25$

|  | $\mathbf{N H}_{\mathbf{4}}{ }^{+}$ | $\rightleftharpoons$ | $\mathbf{H}_{\mathbf{3}} \mathbf{O}^{\mathbf{+}}$ | $\mathbf{N H}_{\mathbf{3}}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.500 |  | 0 | 0.500 |
| $\mathbf{C}$ | -x |  | +x | +x |
| $\mathbf{E}$ | $0.500-\mathrm{x}$ |  | X | $0.500+\mathrm{x}$ |

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{a}\left[\mathrm{NH}_{4}^{+}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(5.6 \times 10^{-10}\right)(0.500 \not-x)}{(0.500+x)}=5.6 \times 10^{-10} \mathrm{M}
$$

$$
\mathrm{pH}=-\log \left(5.6 \times 10^{-10}\right)=9.25
$$

## Beaker 3

$100 \mathrm{~mL} 1.0 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}$ and $100 \mathrm{~mL} 1.0 \mathrm{M} \mathrm{NaHCO}_{3}$
$\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})$
$K_{\mathrm{a}}$ of $\mathrm{H}_{2} \mathrm{CO}_{3}=4.4 \times 10^{-7} \quad \mathrm{pK}_{\mathrm{a}}$ of $\mathrm{H}_{2} \mathrm{CO}_{3}=\underline{6.36}$

## Beaker 2

100 mL 1.0 M HF and 100 mL 1.0 M NaF
$\mathbf{H F}(\mathrm{aq})+\mathrm{H}_{2} \mathbf{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{F}^{-}(\mathrm{aq})$
$K_{\mathrm{a}}$ of $\mathrm{HF}=3.5 \times 10^{-4} \quad \mathrm{pK}_{\mathrm{a}}$ of $\mathrm{HF}=3.46$

|  | $\mathbf{H F}$ | $\rightleftharpoons$ | $\mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}$ | $\mathbf{F}^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.500 |  | 0 | 0.500 |
| C | -x |  | +x | +x |
| $\mathbf{E}$ | $0.500-\mathrm{x}$ |  | X | $0.500+\mathrm{x}$ |

$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{F}^{-}\right]}{[\mathrm{HF}]} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{a}[\mathrm{HF}]}{\left[\mathrm{F}^{-}\right]}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(3.5 \times 10^{-4}\right)(0.500 \not-x)}{(0.500+x)}=3.5 \times 10^{-4} \mathrm{M}$
$\mathrm{pH}=-\log \left(3.5 \times 10^{-4}\right)=3.46$

## Beaker 4

100 mL 1.0 M HF and 300 mL 1.0 M NaF
$\mathbf{H F}(\mathbf{a q})+\mathbf{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{F}^{-}(\mathrm{aq})$
$K_{\mathrm{a}}$ of $\mathrm{HF}=3.5 \times 10^{-4} \quad \mathrm{pK}_{\mathrm{a}}$ of $\mathrm{HF}=3.46$

|  | $\mathbf{H}_{\mathbf{2}} \mathbf{C O}_{\mathbf{3}}$ | $\rightleftharpoons$ | $\mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}$ | $\mathbf{H C O}_{\mathbf{3}}{ }^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.500 |  | 0 | 0.500 |
| $\mathbf{C}$ | -x |  | +x | +x |
| $\mathbf{E}$ | $0.500-\mathrm{x}$ |  | X | $0.500+\mathrm{x}$ |

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{a}\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(4.4 \times 10^{-7}\right)(0.500 \not-x)}{(0.500 \times x)}=4.4 \times 10^{-7} \mathrm{M}}
\end{aligned}
$$

|  | $\mathbf{H F}$ | $\rightleftharpoons$ | $\mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}$ | $\mathbf{F}^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.250 |  | 0 | 0.750 |
| C | -x |  | +x | +x |
| $\mathbf{E}$ | $0.250-\mathrm{x}$ |  | X | $0.750+\mathrm{x}$ |

$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{F}^{-}\right]}{[\mathrm{HF}]} ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{a}[\mathrm{HF}]}{\left[\mathrm{F}^{-}\right]}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(3.5 \times 10^{-4}\right)(0.250 \not-x)}{(0.750+x)}=1.2 \times 10^{-4} \mathrm{M}$

$$
\mathrm{pH}=-\log \left(4.4 \times 10^{-7}\right)=6.36
$$

$\mathrm{pH}=-\log \left(1.2 \times 10^{-4}\right)=3.93$
9. Model 2 describes four buffer solutions, each consisting of a weak acid and its conjugate base. Using the given $\mathrm{K}_{\mathrm{a}}$ of each acid, calculate the $\mathrm{pK}_{\mathrm{a}}$ of each acid and fill in values above each ICE chart.
10. Fill in the ICE charts using " $x$ 's" where needed. (Be careful--watch out for dilution effects when determining initial concentrations.) Then, underneath each ICE chart, write the $\mathrm{K}_{\mathrm{a}}$ expression. Then, rearrange the $\mathrm{K}_{\mathrm{a}}$ expression to solve for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$(no numbers yet!). Then, plug in values from the ICE chart and obtain the numerical value of $\left[\mathbf{H}_{3} \mathbf{O}^{+}\right]$. In addition, determine the $\mathbf{p H}$ of each solution.
11. Do all buffers solutions have a neutral pH ? No Justify your answer with data from Model 2.
The buffer systems have pH values from acidic (HF) to basic $\left(\mathrm{NH}_{4}{ }^{+}\right)$.
12. When a buffer system consists of equal concentrations of a weak acid and its conjugate base, how does the $\mathrm{p} K_{\mathrm{a}}$ value of the weak acid compare to the pH of the solution? The $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$

