## 1. Buffers

## Buffers

An acid-base buffer is a solution that resists changes in pH following the addition of relatively small amounts of a strong acid or base.

Example: Consider a solution of 1.0 M acetic acid.

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}
$$

- Acetic acid is a weak acid - only a small percent of the weak acid is ionized

|  | $\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}$ | + | $\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$ | $\leftrightharpoons$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 1.0 M |  | -- |  | 0 M | 0 M |  |
| $\mathbf{C}$ | -x |  | -- |  | +x |  | +x |
| $\mathbf{E}$ | $1.0 \mathrm{M}-\mathrm{x}$ |  | -- |  | x |  | x |

$$
\mathrm{K}_{\mathrm{a}}=
$$

[ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right]$
$\left[\mathrm{CH}_{3} \mathrm{COO}-\right]$

If a strong base was added to a solution, acetic acid will be there to neutralize the base.

If a strong acid was added, there would be no species to neutralize it.

In order for a buffer solution to be effective, EQUIVALENT CONCENTRATIONS of a weak acid and a conjugate base must be in solution.

A regular acetic acid solution...

An acetic acid buffer solution...

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}
$$

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{\text {(aq) }}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{\text {(aq) }}
$$

Consider the following pairs of solutions:
a) Circle the pairs of chemical species below that could be used to prepare a buffer solution.
b) For the pairs that you circled, write the buffer equation.

| $\mathrm{HNO}_{3}$ and $\mathrm{NaNO}_{3}$ | KF and HF | $\mathrm{HNO}_{2}$ and $\mathrm{HNO}_{3}$ | HCOOH and LiHCOO |
| :---: | :---: | :---: | :---: |
| $\mathrm{NaHSO}_{4}$ and $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | $\mathrm{~K}_{2} \mathrm{CO}_{3}$ and $\mathrm{K}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ | HCl and NaCl | $\mathrm{KH}_{2} \mathrm{PO}_{4}$ and $\mathrm{K}_{2} \mathrm{HPO}_{4}$ |

## (Acid) Buffer Equation:

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}
$$

Because ...
Then ...

Or in general...

The hydronium ion concentration (and therefore the pH ) of a buffer solution depends on:

1. the $\mathrm{K}_{\mathrm{a}}$ value.
2. the ratio of the concentration of the weak acid to its conjugate base.

Using our acetic acid example...

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}
$$

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

$$
\mathrm{pH}=
$$

## Now, let's shift our system!

We now add 0.10 mol HCl to 1.0 M buffer solution with no volume change.

- Would we expect the pH to decrease or increase?
- Would the system shift left or right?

$$
\begin{array}{cc}
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})
\end{array} \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})} 1.0 \mathrm{M}
$$

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

$$
\mathrm{pH}=
$$

We now add 0.10 mol NaOH to 1.0 M buffer solution with no volume change.

- Would we expect the pH to decrease or increase?
- Would the system shift left or right?

$$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \leftrightharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \\
1.0 \mathrm{M} \\
1.0 \mathrm{H}
\end{gathered}
$$

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

$$
\mathrm{pH}=
$$

Add 0.10 M HCl
Add 0.10 M NaOH
Unbuffered System $\mathrm{pH}=$

Add 0.10 M HCl


Buffer System $\mathrm{pH}=$

Add 0.10 M NaOH


## Practice.

Consider a 1.0 M hydrofluoric acid buffer system.
a. What is the equation?
b. Calculate the pH of an undisturbed system.
c. Calculate the pH when 0.050 M hydrobromic acid is added to the original buffer system.
d. Calculate the pH when $0.050 \mathrm{M} \mathrm{Mg}(\mathbf{O H})_{2}$ is added to the original buffer system.

