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1a. A buffer solution is constructed from a weak acid and its conjugate base such that both are present in substantial concentrations. List two example buffer solutions. Write a chemical equation that represents the equilibrium on which the buffer is based.

Example buffer systems: $\mathbf{H C}_{\mathbf{2}} \mathbf{H}_{3} \mathbf{O}_{2}(a q) / \mathbf{C}_{2} \mathbf{H}_{3} \mathrm{O}_{2^{-}}{ }^{-}(a q)$ and $\mathbf{N H}_{3}(a q) / \mathbf{N H}_{4}{ }^{+}(a q)$

$$
\begin{aligned}
\mathbf{H C}_{2} \mathbf{H}_{\mathbf{3}} \mathbf{O}_{\mathbf{2}}(a q) & \rightleftharpoons \mathbf{H}^{+}(a q)+\mathbf{C}_{2} \mathbf{H}_{3} \mathbf{O}_{2^{-}}^{-(a q)} \\
\mathbf{N H}_{\mathbf{3}}(a q)+\mathbf{H}_{\mathbf{2}} \mathrm{O}(l) & \rightleftharpoons \mathbf{N H}_{\mathbf{4}^{+}(a q)}+\mathbf{O H}^{-}(a q)
\end{aligned}
$$

b. Use one of your examples from the previous question to describe how the pH of the solution would be effected by the addition of a small amount of acid. (Hint: Use Le Chatelier's Principle in your explanation.)

$$
\mathbf{H}^{+}(a q) \quad+\mathbf{C}_{2} \mathbf{H}_{3} \mathbf{O}_{2^{-}}^{-(a q)} \rightleftharpoons \mathbf{H C}_{2} \mathbf{H}_{\mathbf{3}} \mathbf{O}_{2}(a q)
$$

Adding a small amount of acid to a solution containing a weak acid and its conjugate base, will result in the small amount of acid reacting with the base component of the buffer to reduce the base component of the buffer by a small amount and increasing the acid component of the buffer by a small amount. The result will change the ratio of $\frac{\mathrm{HC}_{2} \mathbf{H}_{3} \mathrm{O}_{\mathbf{2}}}{\mathbf{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}}$by only a small amount with a net result of very little change in the pH of the buffer solution.
c. Use one of your examples from the previous question to describe how the pH of the solution would be effected by the addition of a small amount of base. (Hint: Use Le Chatelier's Principle in your explanation.)

$$
\mathrm{OH}^{-}(a q) \quad+\mathrm{HC}_{2} \mathbf{H}_{3} \mathrm{O}_{2}(a q) \rightleftharpoons \mathrm{C}_{2} \mathbf{H}_{3} \mathrm{O}_{2}^{-}(a q) \quad+\mathrm{H}_{2} \mathrm{O}(l)
$$

Adding a small amount of base to a solution containing a weak acid and its conjugate base, will result in the small amount of base reacting with the acid component of the buffer to decrease the acid component of the buffer by a small amount and increasing the base component of the buffer by a small amount. The result will change the ratio of $\frac{\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}}{\mathbf{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}-}$ by only a small amount with a net result of very little change in the $\mathbf{p H}$ of the buffer solution.
d. Explain how the behavior you described in the previous questions would have been different with an unbuffered solution.

In an unbuffered system addition of a small amount of acid or base may well cause a large change in pH .
e. Explain how a buffered solution consisting of a weak acid and a weak base could be constructed from a weak acid and a strong base or a weak base and a strong acid. Write a chemical equation representing how this can be done.

A buffer solution can be constructed by add half the number of moles of a strong base to a solution of a weak acid. All of the base would react forming a solution with equal amounts of the weak acid and its conjugate base. That is what a buffer solution is.
2. Complete the following problems
a. Calculate the pH of a solution prepared by mixing 20.0 mL of 0.300 M $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ with 20.0 mL of $0.350 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$.

## Dilution calculation:

$$
\begin{aligned}
& {\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.300 \mathrm{M}\left(\frac{20.0 \mathrm{~mL}}{40.0 \mathrm{~mL}}\right)=0.150 \mathrm{M}} \\
& {\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=0.350 \mathrm{M}\left(\frac{20.0 \mathrm{~mL}}{40.0 \mathrm{~mL}}\right)=0.175 \mathrm{M}}
\end{aligned}
$$

|  | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $\rightleftharpoons \mathbf{H}^{+}(a q)$ | $+\mathrm{C}_{2} \mathbf{H}_{3} \mathrm{O}_{2}^{-(a q)}$ | $\mathrm{x}=\left[\mathrm{HC}_{\mathbf{2}} \mathbf{H}_{\mathbf{3}} \mathrm{O}_{\mathbf{2}}\right]_{\text {diss }}$ |
| :---: | :---: | :---: | :---: | :---: |
| I | 0.150 M | $\sim$ | 0.175 M |  |
| C | -x | +x | +x |  |
| E | 0.150 - x | $\mathbf{x}$ | $\mathbf{0 . 1 7 5}+\mathrm{x}$ |  |
|  | $\frac{\left.\mathrm{H}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right.}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right.}$ |  |  |  |

$1.8 \times 10^{-5}=\frac{(\mathbf{x})(0.175+x)}{\underline{0.150}-\mathrm{x}} \quad$ assume $\mathrm{x} \ll 0.150$
$1.8 \times 10^{-5}=\frac{(\mathrm{x})(\mathbf{0 . 1 7 5 )}}{\underline{0.150}}$
$1.54 \times 10^{-5}=x=\left[\mathrm{H}^{+}\right]$
$\mathrm{pH}=4.81$
b. Specify the reagents and the specific concentrations of each reagent needed to prepare a buffer solution which would have a pH of 4.19 .

The optimum buffer solution contains equal concentrations of the weak acid and the conjugate base, or of the weak base and the conjugate acid. Under such circumstances, the following occurs:

|  | HA $\rightleftharpoons$ | $\mathrm{H}^{+}+$ | $\mathrm{A}^{-}$ |
| :---: | :---: | :---: | :---: |
| I | $\mathrm{CHA}^{\text {H }}$ | $\sim$ | $\mathrm{C}_{\text {A }}$ |
| C | -x | +x | $+\mathrm{x} x=\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]_{\text {diss }}$ |
| E | $\mathrm{CHA}_{\text {- }} \mathrm{x}$ | $\mathbf{x}$ | $\mathrm{C}_{\mathrm{A}}+\mathrm{x}$ |
| $\mathbf{K}_{\mathbf{a}}$ | $=\frac{\left[\mathbf{H}^{+}\right]\left[\mathbf{A}^{-}\right]}{[\mathbf{H A}]}$ |  |  |
| $\mathbf{K}_{\mathbf{a}}$ | $=\frac{(\mathbf{x})\left(\mathbf{C}_{\mathrm{A}}+\mathbf{x}\right)}{\mathbf{C}_{\mathbf{H A}}-\mathbf{x}}$ | $\mathrm{x} \lll<\mathrm{C}_{\mathrm{HA}}$ |  |
| $\mathrm{K}_{\mathrm{a}}$ | $=\frac{(\mathbf{x})\left(\mathbf{C}_{\mathrm{A}}\right)}{\mathbf{C}_{\mathrm{HA}}}$ |  |  |
| Since | $\mathrm{HA}=\mathrm{C}_{\mathrm{A}}$ |  |  |
| $\mathrm{K}_{\mathrm{a}}$ | $=\mathrm{x}=\left[\mathrm{H}^{+}\right]$ |  |  |
| $\mathbf{p K}_{\mathbf{a}}$ | $=\mathbf{p H}$ |  |  |

So, if the pH of the buffer is 4.19 , the $\mathrm{pK}_{\mathrm{a}}$ will be the same if the concentration of the weak acid and the its conjugate base are the same. $\mathrm{pH}=4.19$ so $\mathrm{pK}_{\mathrm{a}}=4.19$
$\mathrm{K}_{\mathrm{a}}=6.46 \times 10^{-5}$
The buffer solution contains equal amounts of benzoic acid $\left(\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right)$ and sodium benzoate ( $\mathrm{NaC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}$ ).

