

Buffer solutions

Buffer solutions

- ◆ Whenever in an aqueous solution there are a weak acid (HA) and its salt (NaA), the two following equilibria are active:



Acidic buffer



- ◆ The same holds when in an aqueous solution there are a weak base (AOH) and its salt (ACl):



Basic buffer



Acidic buffer

- 1) $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$
- 2) $\text{NaA} \rightarrow \text{Na}^+ + \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

For these two equilibria we can calculate a constant and derive the protons concentration:

$$K_a = \frac{[\text{H}_3\text{O}^{+1}][\text{A}^{-1}]}{[\text{HA}]} \qquad [\text{H}_3\text{O}^{+1}] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^{-1}]}$$

At equilibrium:

$[\text{A}^-] = [\text{A}^-]$ from the acid dissociation + $[\text{A}^-]$ from the hydrolysis = C_s
 $[\text{HA}] = [\text{HA}]$ not dissociated + $[\text{HA}]$ reassociated from the salt = C_a
Hence:

$$[\text{H}_3\text{O}^{+1}] = K_a \cdot \frac{C_a}{C_s}$$

Basic buffer

- 1) $\text{AOH} + \text{H}_2\text{O} \rightleftharpoons \text{A}^+ + \text{OH}^-$
- 2) $\text{ACl} \rightarrow \text{Cl}^- + \text{A}^+ + \text{H}_2\text{O} \rightleftharpoons \text{AOH} + \text{H}_3\text{O}^+$

Even for these two equilibria we can calculate a constant and derive the hydroxyls concentration:

$$K_b = \frac{[\text{OH}^{-1}][\text{A}^{+1}]}{[\text{AOH}]} \qquad [\text{OH}^{-1}] = K_b \cdot \frac{[\text{AOH}]}{[\text{A}^{+1}]}$$

At equilibrium:

$[\text{A}^+] = [\text{A}^+]$ base dissociation + $[\text{A}^+]$ from the hydrolysis = C_s
 $[\text{AOH}] = [\text{AOH}]$ not dissociated + $[\text{AOH}]$ reassociated from the salt = C_b

Hence:
$$[\text{OH}^{-1}] = K_b \cdot \frac{C_b}{C_s}$$

How to calculate the pH of buffer solutions

- ◆ If we convert the previous two equations into log → we can derive the Henderson-Hasselback equations:

$$pH = pK_a + \log \frac{C_s}{C_a}$$

For an acidic buffer solution

$$pOH = pK_b + \log \frac{C_s}{C_b}$$

For a basic buffer solution

How does a buffer solution work?

- ◆ The presence of two opposite equilibria in the same solution at the same time, makes possible to neutralize the incoming protons/hydroxyls, which would otherwise perturb the water equilibrium

Let's add HCl to an acidic buffer and see what happens:

The ratio $[H_3O^+]/[OH^-]$ remains constant



Exercise 1

- ◆ 1 meq of HCl is added to 1L of a solution made by acetic acid 0.1 M and sodium acetate 0.1 M. Calculate the pH of the buffer solution before and after having added the acid ($K_a = 1.8 \cdot 10^{-5} \text{M}$).



In solution there is a weak acid and its salt \rightarrow we have an acidic buffer solution, we can use the Henderson-Hasselback formula to calculate the pH:

$$pH = pK_a + \log \frac{C_s}{C_a} = -\log(1.8 \cdot 10^{-5}) + \log \frac{0.1}{0.1} = 4.74$$

1 meq of HCl in 1 L gives a total protons concentration
 $\rightarrow [\text{H}_3\text{O}^+] = 10^{-3} / 1 = 10^{-3} \text{ N}$

Adding protons to equilibrium 1) \rightarrow **Ca increases**;
Adding protons to equilibrium 2) \rightarrow **Cs decreases**;
Both change by the same amount of protons added

- ◆ Thereby we can use the same equation but with the new quantities:

$$pH = pK_a + \log \frac{C_s - [\text{H}_3\text{O}^+]}{C_a + [\text{H}_3\text{O}^+]} = 4.74 + \log \frac{0.1 - 0.001}{0.1 + 0.001} = 4.73$$

The pH has varied by 0.01 units ONLY

What would have happened if we were to add 1 meq of HCl to 1L of water?

At the beginning $\text{pH} = 7.0$

Then in solution there is: $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

Hence $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 10^{-3} = 3.0$

The pH has changed by 4.0 units