Teacher's Tools® Chemistry

Acid Base Chemistry: Buffers: Student Review Notes
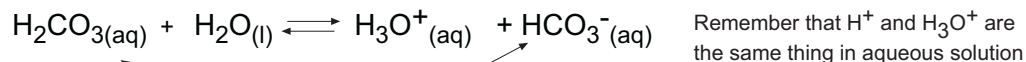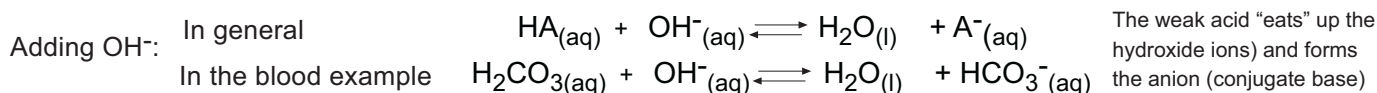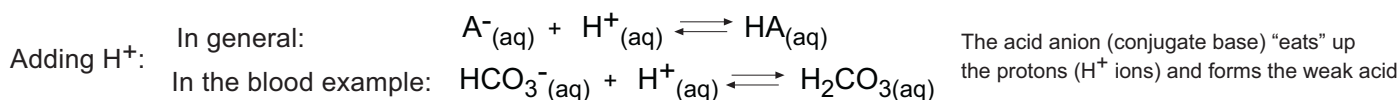
Overview

Buffers are solutions that have the special property of maintaining **a relatively constant pH**.

A good example of a buffer is your blood and within this very complex aqueous solution, the presence of carbonic-acid and bicarbonate ion "buffers" the pH around a value of 7.4. Take a look at the equilibrium between these two molecules:

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-_{(aq)}$$

Remember that H^+ and H_3O^+ are the same thing in aqueous solution

Notice that it's an equilibrium between a weak acid and its anion (conjugate base).

Buffers are aqueous solutions that contain relatively equal amounts of a conjugate acid-base pair. They are resistant to a change in pH because of this equilibrium and the reactions that occur upon the addition of small amounts of H^+ or OH^-. Take a look:

Adding H^+:

In general: $\quad A^-_{(aq)} + H^+_{(aq)} \rightleftharpoons HA_{(aq)}$

In the blood example: $\quad HCO_3^-_{(aq)} + H^+_{(aq)} \rightleftharpoons H_2CO_{3(aq)}$

The acid anion (conjugate base) "eats" up the protons (H^+ ions) and forms the weak acid

Adding OH^-:

In general $\quad HA_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} + A^-_{(aq)}$

In the blood example $\quad H_2CO_{3(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} + HCO_3^-_{(aq)}$

The weak acid "eats" up the hydroxide ions) and forms the anion (conjugate base)

The amount of H+ or OH- that a buffer can absorb without a significant change in the pH of the solution is called the **Buffer Capacity**. This has everything to do with the amount of weak acid/conjugate base that is in the solution.

Henderson-Hasselbach Equation

The fundamental equation for buffer chemistry is the **Henderson-Hasselbach equation** (H-H equation) and it comes right from the equilibrium expression for a weak acid. Take a look:

$$HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$
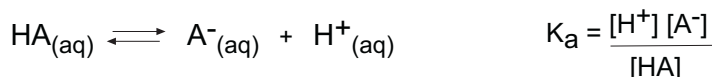
"p" the whole K_a expression and use the product to sum property of logarithms

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

solve for pH and you have the **Henderson Hasselbach equation**

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Note that the ratio in the H-H equation is volume independent. You can use a ratio of moles or molar concentrations.

pH = pKa is where you start selecting an acid/conjugate base pair for a solution that will buffer at a desired pH.

It is the ratio of acid anion to weak acid that alters the solution pH from the pKa of the weak acid. This ratio is the thing that changes with the addition of H^+ or OH^- and how much it changes with the addition of these species is the buffer capacity. Take a look at some weak acid/acid anion pairs and where the buffer pH would start:

Weak Acid/Conjugate Base	K_a	pK_a = pH for a ratio of 1
HCN/CN^-	4.0×10^{-10}	9.4
NH_4^+/NH_3	5.6×10^{-10}	9.25
H_2CO_3/HCO_3^-	4.4×10^{-7}	6.36
$HC_2H_3O_2/C_2H_3O_2^-$	1.8×10^{-5}	4.82

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Preparing a Buffer

There are two ways to make a buffer solution. The first thing you need to decide on is the pH about which you want to buffer and choose an appropriate weak acid based on its K_a value.

Method 1: Add equal amounts of a weak acid and a salt that contains the acid anion.

Example: How many moles of sodium bicarbonate ($NaHCO_3$) should be added to one liter of 0.100 M carbonic acid (H_2CO_3) in order to make a buffer with a pH = 7.00? Ka = 4.2×10^{-7} for H_2CO_3.

The weak acid is H_2CO_3 and the conjugate base is HCO_3^-

According to the Henderson-Hasselbach equation:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{for this problem,} \quad pH = 7.00 = -\log(4.2 \times 10^{-7}) + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$0.623 = \log \frac{[HCO_3^-]}{0.100}$$

$[HCO_3^-] = 0.42$ M. You therefore need to add .42 moles to 1 L of solution

Method 2: Add half as many moles of a strong base to a weak acid solution.

Example: What is the pH of a buffer solution made from addition 0.100 moles of NaOH to 1 L of a solution that is 0.200 M in HCN? Ka = 4.0×10^{-10} for HCN.

The strong base reacts with the weak acid and completely reacts. What is left behind is a solution of the weak acid, HCN, and its conjugate base (the acid anion, CN^-), i.e. a buffer.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad \text{for this problem,} \quad pH = -\log(4.0 \times 10^{-10}) + \log \frac{[CN^-]}{[HCN]}$$

$$pH = -\log(4.0 \times 10^{-10}) + \log \frac{0.100}{0.100}$$

$$pH = pK_a = -\log(4.0 \times 10^{-10}) = 9.40$$

When the concentration of weak acid and its conjugate base are equal, the log term in the H-H equation is equal to zero (log(1) = 0). Remember this for acid-base titration. At the half-equivalence point of a titration, the point at which half of the species in solution has been neutralized, the pH = PK_a, if the solution is a weak acid.

One thing that is very convenient about the H-H equation is that it works in cases where you have an aqueous solution that contains a weak acid and its anion **even if the solution is not a buffer** (i.e., does not have a significant buffer capacity).

The H-H equation is derived from the equilibrium expression—therefore it has to hold and is a much shorter way to get equilibrium concentrations than using an ICE table.