BUFFER SELECTION

- Buffer pH is controlled by the pKa of the acidic species in the buffer.

$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

- Choose a buffer system so that the desired pH is within +/- 1 pH unit of the pKa

- You also need to ensure that the components of the buffer do not interact with your chemistry!

BUFFER PREPARATION

- many buffers are prepared by mixing specific amounts of both components of the Buffer system (acid / conjugate base or base / conuugate acid)

Some buffer "recipes" call for making the conjugate ion FROM the weak acid or base ... by adding a STRONG acid or base!

$$NH_3 + HNO_3 \longrightarrow NH_4^+ + NO_3^-$$

The reaction of the strong acid with the weak base goes essentially to completion!

If you have more ammonia than nitric acid, you will end up with a solution containing a significant amount of both ammonia and ammonium ion ... a buffer!

BUFFER CAPACITY

- A buffer is good only as long as there is a significant concentration of both the acidic and basic species

- buffer capacity: how much acid or base can a buffer resist before losing its ability to buffer

- Buffer pH depends on the RATIO of acid to base!

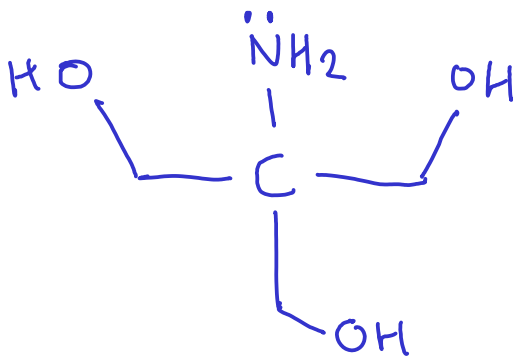
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

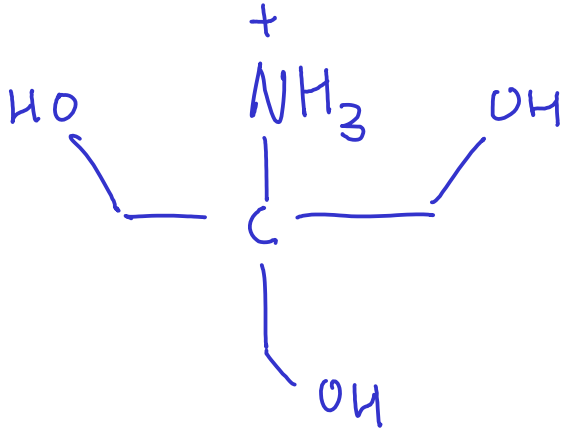
Ratio determines pH; the actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A- , it will have the same pH as a buffer with 2.0M HA and 2.0M A- .... but the 2M buffer will have a higher BUFFER CAPACITY - it will resist more additions of acid or base.

Buffer calculation: Tris buffer - Tris(hydroxymethyl)-aminomethane



tris base



tris-HCl (conjugate acid of tris base)

$pK_a = 8.06$

Calculate the pH of a buffer made from 50 mL of 0.10M tris and 50 mL of 0.15M tris-HCl. Assume volumes add.

$$pH = pK_{a,\text{acidic}} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

[tris]: $M_1V_1 = M_2V_2$ $(0.10\,M)(50.0\,mL) = M_2(100.0\,mL)$

$[\text{tris}] = M_2 = 0.050\,M$

[tris-HCl]: $M_1V_1 = M_2V_2$ $(0.15\,M)(50.0\,mL) = M_2(100.00\,mL)$

$[\text{tris-HCl}] = 0.075\,M$

$$pH = 8.06 + \log\left(\frac{0.050}{0.075}\right) = 7.88$$

Take 100. mL of the previous buffer (0.05 M tris / 0.075 M tris-HCl), and add 5.0 mL of 0.10 M HCl. What is the pH of the mixture?

The HCl reacts with the tris base, converting it to tris-HCl

$$tris + H_3O^+ \longrightarrow tris\text{-}H^+ + H_2O$$

$$(tris + HCl \longrightarrow tris\text{-}HCl)$$

We need to find the new concentrations of each species in this buffer system. Remember also that we DILUTED the system by adding HCl

SPECIES	INITIAL mmol	CHANGE IN REACTION	FINAL mmol	CONCENTRATION
tris	100 mL x 0.05 M = 5.0 mmol	−0.5 mmol	4.5 mmol	$\frac{4.5\ mmol}{105\ mL} = 0.0428571\ M$
tris-H+	100 mL x 0.075 M = 7.5 mmol	+0.5 mmol	8.0 mmol	$\frac{8.0\ mmol}{105\ mL} = 0.0761905\ M$
HCl	5 mL x 0.10 M = 0.5 mmol	−0.5 mmol	0 mmol	0

Now, find the pH of the solution using the Henderson-Hasselbalch equation:

$$pH = 6.06 + \log\left(\frac{0.0428571}{0.0761905}\right) = \boxed{7.81}$$

The pH of the original buffer was 7.88, so the pH has decreased by 0.07 pH units.

Compare this 0.07 unit pH change with adding 5.0 mL of 0.10 M HCl to 100. mL of pure water.

$M_1V_1 = M_2V_2$

$(0.10\ M)(5.0\ mL) = M_2(105\ mL)$

$0.0047619\ \underline{M}\ HCl = [H_3O^+]$

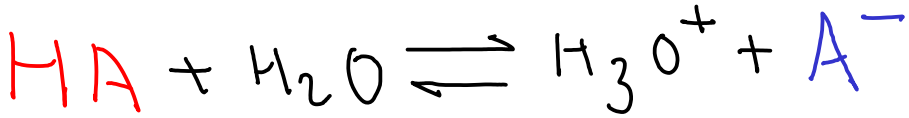
So, $pH = \underline{\underline{2.32}}$ ... which is a change of 4.68 pH units from water's original pH of 7.00!

INDICATORS

-Instead of using a pH meter to monitor acidity, we may choose to use an acid-base INDICATOR.

- Acid-base indicators are weak acids or weak bases which are highly colored.

- The color of the undissociated indicator MUST BE DIFFERENT than the color of the dissociated form!



The indicator must be present in very low concentrations - so that the indicator's equilibrium DOES NOT CONTROL the pH of the solution!

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

$$pH = pK_{a,ind} + \log\left(\frac{[A^-]}{[HA]}\right)$$

When does the color of the indicator change?

IF the pH is << pKa, then the log term above must be both large AND negative!

- What color is the solution?

$[HA] >> [A^-]$ ... so the SOLUTION IS RED!

If the pH is >> pKa, then the log term above must be both large AND positive!

- What color is the solution?

$[A^-] >> [HA]$ ... so the SOLUTION IS BLUE!

- So, the color changes when the pH of the solution is near the pKa of the indicator, BUT we can only DETECT the change when enough of the other form is present.