

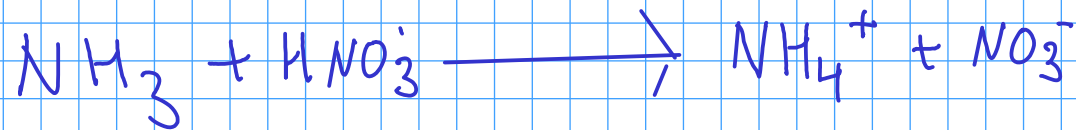
## BUFFER SELECTION

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

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

- 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!

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



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!

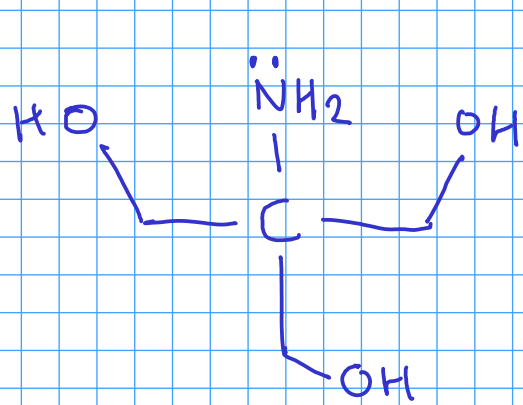
$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right)$$

Henderson-  
Hasselbalch  
Equation

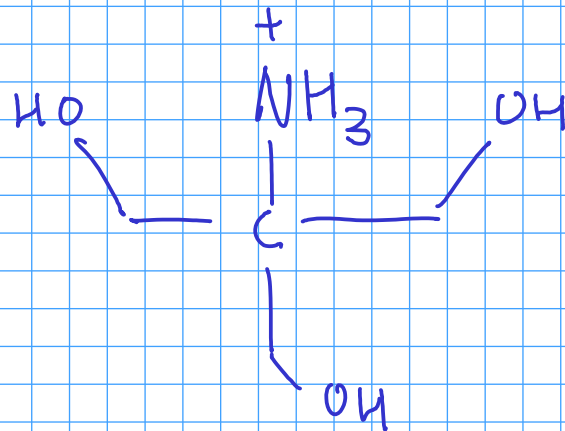
Ratio determines pH; the  
actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A<sup>-</sup>, it will have the same pH as a buffer with 2.0M HA and 2.0M A<sup>-</sup> ... 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

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

$$[\text{tris}]: m_1 V_1 = m_2 V_2 \quad (0,10 \text{ M})(50 \text{ mL}) = m_2 (100 \text{ mL}) \\ = 0,05 \text{ M}$$

$$[\text{tris-HCl}]: m_1 V_1 = m_2 V_2 \quad (0,15 \text{ M})(50 \text{ mL}) = m_2 (100 \text{ mL}) \\ = 0,075 \text{ M}$$

$$pH = 8,06 + \log \left( \frac{0,05 \text{ M}}{0,075 \text{ M}} \right) = 7,88$$

Take 100. mL of the previous buffer (0.05 M tris / 0.075 M tris-HCl), and add 5.0 mL of .10 M HCl. What is the pH of the mixture?

The HCl would react with the tris base, forming tris-HCl



Calculate the new concentrations of everything in the solution

	initial millimoles	$\Delta$	Final mmol	<u>M</u>
Tris:	$100\text{ mL} \times 0.05\text{ M} = 5\text{ mmol}$	$-0.5\text{ mmol}$	$4.5\text{ mmol}$	$\frac{4.5\text{ mmol}}{105\text{ mL}} = 0.0429$
Tris-HCl:	$100\text{ mL} \times 0.075\text{ M} = 7.5\text{ mmol}$	$+0.5\text{ mmol}$	$8.0\text{ mmol}$	$\frac{8.0\text{ mmol}}{105\text{ mL}} = 0.0762$
HCl:	$5\text{ mL} \times 0.1\text{ M} = 0.5\text{ mmol}$	$-0.5\text{ mmol}$	$0\text{ mmol}$	0

Now, we can find pH using the Henderson-Hasselbalch equation.

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

$$\text{pH} = 8.06 + \log\left(\frac{0.0429}{0.0762}\right) = \boxed{7.81}$$

The pH of the original buffer was 7.88, so the pH 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.

$$M_1 V_1 = M_2 V_2$$

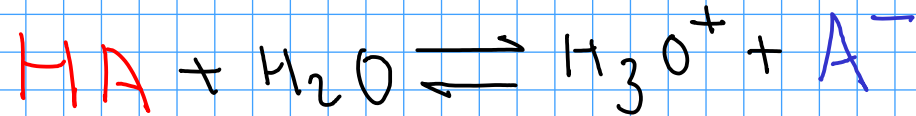
$$(0.10 \text{ M})(5.0 \text{ mL}) = M_2 (105 \text{ mL})$$

$$M_2 = 0.0047619 \text{ M HCl} = [\text{H}_3\text{O}^+]$$

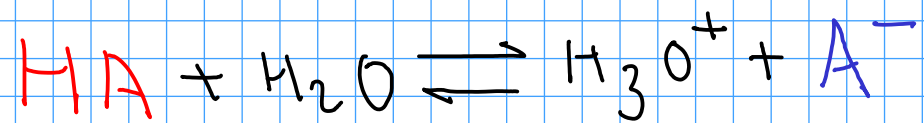
$$\text{pH} = \underline{\underline{2.32}} \quad \dots \text{ which is a change of 4.68 pH units from the original water pH of 7.00!}$$

## 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!



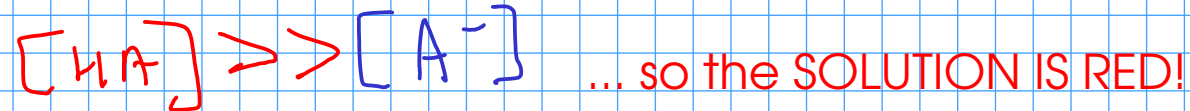
Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

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

When does the color of the indicator change?

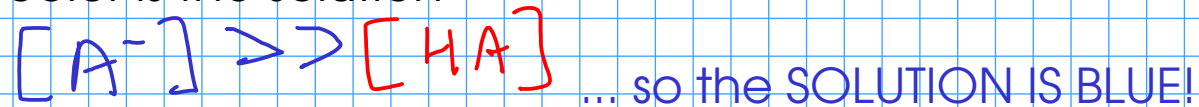
IF the pH is  $\ll$  pKa, then the log term above must be both large AND negative!

- What color is the solution?



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

- What color is the solution?



- 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.