BUFFERS

- resist pH change caused by either the addition of strong acid/base OR by dilution

Made in one of two ways:

$HC_2H_3O_2$ $NaC_2H_3O_2$

① Make a mixture of a weak acid and its conjugate base (as the SALT)

NH_3 NH_4Cl

② Make a mixture of a weak base and its conjugate acid (as the SALT)

For a weak acid, you would:

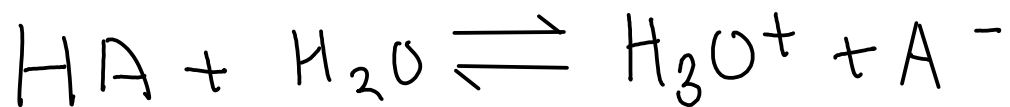$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- Add HA (weak acid)

- Add a salt containing A^- (example: NaA)

- This solution actually contains an acid and a base at equilibrium, with a significant concentration of BOTH.

- The acid in the buffer can neutralize bases, while the base can neutralize acids.

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

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

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

Henderson-Hasselbalch Equation

$[A^-]$ ... from the salt

$[HA]$ ... from the weak acid

- We ASSUME that the initial concentrations of both the acid and its conjugate are equal to the equilibrium concentrations. Valid IF there are significant amounts of both species initially.

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

Henderson-Hasselbalch Equation

ex: acidic buffer

$HC_2H_3O_2$ / $NaC_2H_3O_2$

$$pH = pK_{a, HC_2H_3O_2} + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

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ex: basic buffer

NH_3 / NH_4NO_3

$$pH = pK_{a, NH_4^+} + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$pK_a + pK_b = 14.00$$

... is the -log of $K_a \times K_b = K_w$

Calculate the pH of a buffer made from 3.2 grams of ammonium chloride and 29 mL of 18.1 M ammonia diluted to 50.0 mL with water.

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

Henderson-Hasselbalch Equation

To solve this problem, we need concentrations of ammonia (the base) and ammonium ion (the acid)!

$[NH_3]$: $M_1V_1 = M_2V_2$ Dilution equation!

$$(18.1M)(29mL) = M_2(50.0mL)$$

$$M_2 = 10.498 \underline{M} \; NH_3$$

$[NH_4^+]$:

N: 1 × 14.01
H: 4 × 1.008
Cl: 1 × 35.45
53.492 g/mol

$$3.2_g \; NH_4Cl \times \frac{\text{mol } NH_4Cl}{53.492_g \; NH_4Cl} \times \frac{1}{0.0500L} = 1.19644 M \; NH_4Cl$$

$$= 1.19644 \underline{M} \; NH_4^+$$

pK_{a, NH_4^+}: $K_{b, NH_3} = 1.8 \times 10^{-5}$, so $pK_b = 4.745$

$14.00 = pK_a + pK_b$, $pK_a = 14.00 - 4.745 = 9.255$

$$pH = 9.255 + \log\left(\frac{10.498}{1.19644}\right) = 10.198 \approx 10.20$$

$$0.943$$

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!

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

$$NH_3 + HNO_3 \longrightarrow NH_4^+ + NO_3^-$$
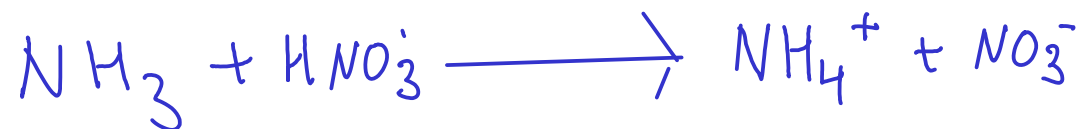
If you have more ammonia than nitric acid, you will end up with a solution containing a significant amount of both ammonia and ammonium ion ... a buffer!

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!

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

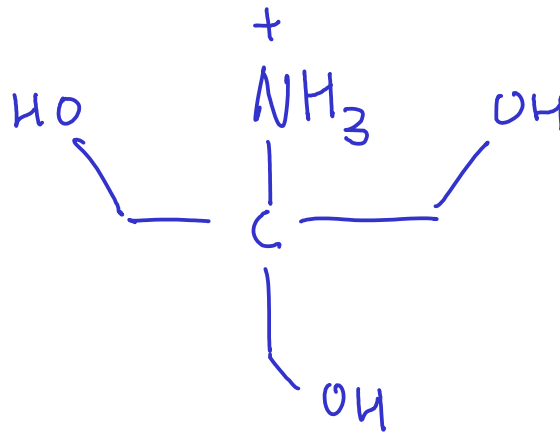Henderson-Hasselbalch Equation

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
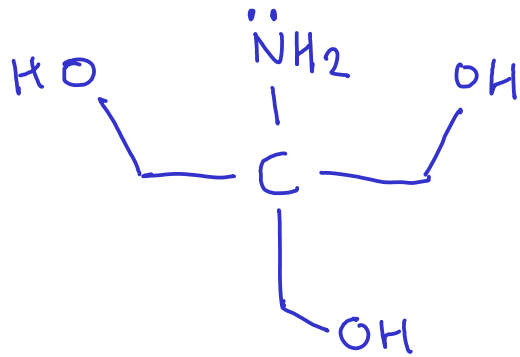
tris base | tris-HCl (conjugate acid of tris base)

$pka = 8,06$

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

$$pH = pKa_{,acidic} + log\left(\frac{[basic\ species.]}{[acidic\ species]}\right)$$

$[tris]$: $m_1 V_1 = m_2 V_2$
$(0.10m)(50mL) = m_2(100mL)$; $m_2 = 0.050m$

$[tris-HCl]$: $m_1 V_1 = m_2 V_2$
$(0.15m)(50mL) = m_2(100mL)$; $m_2 = 0.075m$

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

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

$$tris + HCl \longrightarrow tris-HCl$$

We need to find the new concentrations of species in the buffer AFTER adding the acid:

Species	Initial millimoles	Δ in rxn	Final mmol	Concentration
tris	100 mL × 0.05 M = 5.0 mmol	−0.5 mmol	4.5 mmol	$\frac{4.5 \text{ mmol}}{105 \text{ mL}} = 0.042857$ M
tris-HCl	100 mL × 0.075 M = 7.5 mmol	+0.5 mmol	8.0 mmol	$\frac{8.0 \text{ mmol}}{105 \text{ mL}} = 0.076190$ M
HCl	5 mL × 0.10 M = 0.5 mmol	−0.5 mmol	0 mmol	0

Now, find pH using the Henderson-Hasselbalch equation:

$$pH = 8.06 + \log\left(\frac{0.042857}{0.076190}\right) = \boxed{7.81}$$

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.

$$M_1 V_1 = M_2 V_2$$

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

$$M_2 = 0.0047619 \ \underline{M} \ HCl = [H_3O^+]$$

$$pH = 2.32$$

... which is a change of 4.68 pH units from the original water pH of 7.00 !