Calculate the pH of a buffer made from 30.2 grams of ammonium chloride and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

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

acid: $NH_4^+$ base: $NH_3$ ; $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

To use the H-H equation, we need to know the nominal concentration of both the acid (ammonium ion) and the base (ammonia)

$[NH_3] = ?$ $M_1V_1 = M_2V_2$ The ammonia is DILUTED to make the buffer.

$(18.1\ M)(29\ mL) = M_2(150.\ mL)$

$3.499333333\ M = M_2$

$[NH_4^+] = ?$

$NH_4Cl$: N: $1 \times 14.01$, H: $4 \times 1.008$, Cl: $1 \times 35.45$ = $53.492\ g\ NH_4Cl/mol$

$$30.2\ g\ NH_4Cl \times \frac{mol\ NH_4Cl}{53.492\ g\ NH_4Cl} = 0.564570403\ mol$$

$$[NH_4^+] = \frac{0.564570403\ mol}{0.150\ L} = 3.763802687\ M\ NH_4^+$$

$K_b = 1.8 \times 10^{-5}$ ; $K_a = 5.56 \times 10^{-10}$ ; $pK_{a,NH_4^+} = 9.26$

$$pH = 9.26 + \log\left(\frac{3.499333333\ M\ NH_3}{3.763802687\ M\ NH_4^+}\right) = \boxed{9.22}$$

# 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!

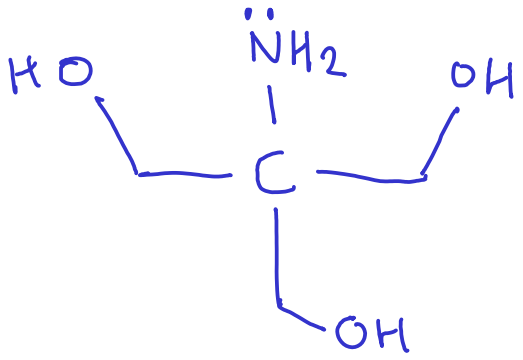
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

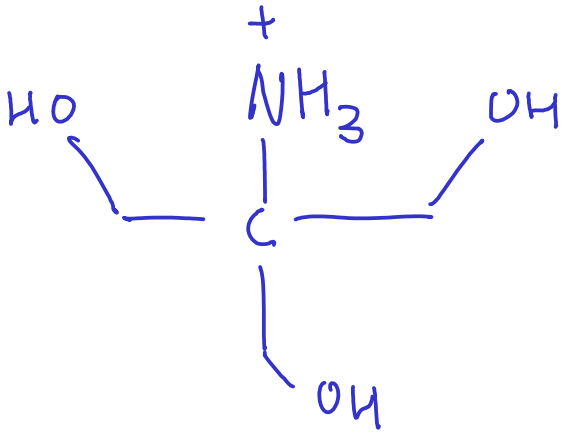
Ratio determines pH; the actual concentrations don't!

- 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)

$Cl^-$

**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. Assume volumes add.

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

[tris]: $M_1V_1 = M_2V_2$ $(0.10\ M)(50.\ mL) = M_2(100.\ mL)$

$M_2 = 0.050\ M$ tris

[tris-HCl]: $(0.15\ M)(50.\ mL) = M_2(100.\ mL)$

$M_2 = 0.075\ M$ tris-HCl

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

Take 100. mL of the previous buffer (0.050 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 should react with the BASIC component of the buffer (tris), changing it to its conjugate acid (tris-H+)

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

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

We need to find out the new concentrations of tris and tris-HCl after reaction!

| Species | Initial mmol | Δ in rxn | Final mmol | Concentration |
|---|---|---|---|---|
| tris | 100 mL x 0.050 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 | 5.0 mL x 0.10 M = 0.5 mmol | −0.5 mmol | 0 mmol | 0 |

Note: The volume of the solution is now 105 mL (due to the added volume of the HCl solutio

Now, use H-H to find pH:

$$pH = 8.06 + \log\left(\frac{0.0428571\ M}{0.0761905\ M}\right) = \boxed{7.81}$$

The original pH was 7.88, so there is a decrease of 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.

$M_1V_1 = M_2V_2$

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

$M_2 = 0.00476190\overline{48}\ M\ HCl$

Strong acid, so hydronium concentration equals acid concentration

$[H_3O^+] = 0.00476190\overline{48}\ M$

$\boxed{pH = 2.32}$

... which is change of 4.68 pH units from water's original pH of 7.00!