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

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 $K_a \times K_b = K_w$

170 Calculate the pH of a buffer made from 30.2 grams of ammonium chloride (FW = 53.492 g/mol) 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

We need to find (1) the pKa of the ammonium ion, (2) the concentration of the ammonia, and (3) the concentration of the ammonium ion.

① $K_{b,NH_3} = 1.8 \times 10^{-5}$ (pA-14, Ebbing), $pK_b = 4.74$

so, $pK_{a,NH_4^+} = 14.00 - 4.74 = 9.26$ $(pK_a + pK_b = 14.00)$

② $M_1V_1 = M_2V_2$ (The ammonia is being diluted from 29 mL to 150 mL)

$(18.1\,M)(29\,mL) = M_2(150.\,mL)$; $M_2 = 3.499333333\,M\ NH_3$

③ $30.2\,g\ NH_4Cl \times \frac{mol\ NH_4Cl}{53.492\,g\ NH_4Cl} = 0.564570403\,mol\ NH_4Cl$

$\frac{0.564570403\,mol\ NH_4Cl}{0.150\,L} = 3.763802687\,M\ NH_4Cl$

$= 3.763802687\,M\ NH_4^+$

(150 mL) → 0.150 L

$pH = 9.26 + \log\left(\frac{3.499333333\,M\ NH_3}{3.763802687\,M\ NH_4^+}\right) = \boxed{9.23}$

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!

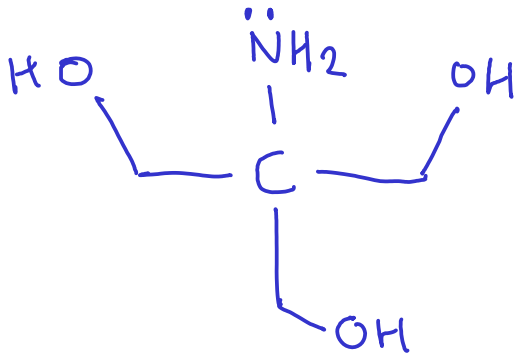
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

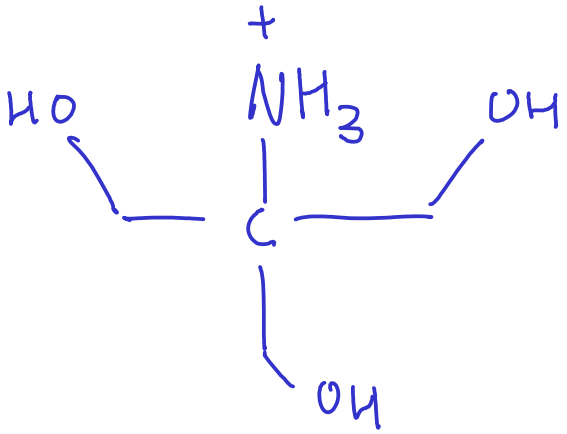
Ratio determines pH; the actual concentrations don't!

- 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]: $M_1V_1 = M_2V_2$ $(0.10M)(50.mL) = M_2(100.mL)$

$M_2 = 0.05M$ tris base

[Tris-HCl]: $M_1V_1 = M_2V_2$ $(0.15M)(50.mL) = M_2(100.mL)$

$M_2 = 0.075M$ tris-HCl

$$pH = 8.06 + \log\left(\frac{0.05M}{0.075M}\right) = 7.88$$