Calculate the pH of a solution which contans 0.10 M ammonia AND 0.10 M ammonium chloride.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-; \quad k_b = 1.8 \times 10^{-5}$$
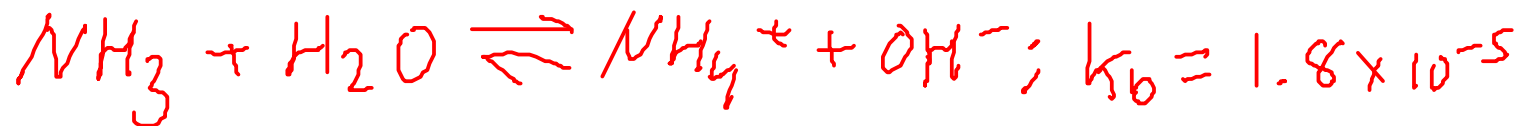
Species	[Init]	Δ	[Equil]
NH_4^+	0.10	$+X$	$0.10 + X$
OH^-	0	$+X$	X
NH_3	0.10	$-X$	$0.10 - X$

$$k_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\frac{(0.10 + x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

Assume 'x' is small relative to 0.10

$$0.10 + x \approx 0.10$$
$$0.10 - x \approx 0.10$$

$$\frac{0.10\, x}{0.10} = 1.8 \times 10^{-5}$$

$$X = 1.8 \times 10^{-5} = [OH^-]$$

$$pOH = -\log_{10}(1.8 \times 10^{-5})$$
$$= 4.74$$

$$So, \quad pH = 14 - 4.74$$

$$\boxed{pH = 9.26}$$

The common-ion effect suppresses the ionization of ammonia, LOWERING the pH relative to the original ammonia solution.

BUFFERS

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

Made in one of two ways:

① Make a mixture of a weak acid and its conjugate base (as the SALT) $HC_2H_3O_2$ $NaC_2H_3O_2$

② Make a mixture of a weak base and its conjugate acid (as the SALT) NH_3 NH_4Cl

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.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
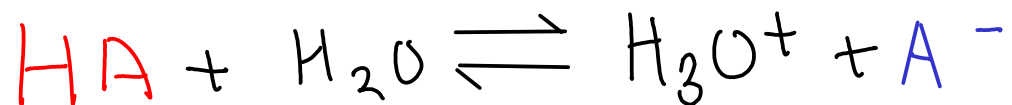
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

$$HC_2H_3O_2 \,/\, NaC_2H_3O_2$$

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

ex: basic buffer

$$NH_3 \,/\, NH_4NO_3$$

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

$$pK_a + pK_b = 14.00 \quad \text{... is the -log of } K_a \times K_b = K_w$$

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 nned to know the concentration of both ammonia (the base) and ammonium ion (the acid) in the buffer!

$[NH_3] = ?$; $M_1 V_1 = M_2 V_2$ $(18.1m)(29.0mL) = M_2(150.mL)$

$m_2 = [NH_3] = 3.50\ M$

$[NH_4^+] = ?$

$30.2g\ NH_4Cl \times \dfrac{mol\ NH_4Cl}{53.492\ g\ NH_4Cl} =$

$= 0.56457\ mol\ NH_4Cl$

$NH_4Cl: \quad N = 1 \times 14.01$
$H: 4 \times 1.008$
$Cl = 1 \times 35.45$
$\overline{53.492\ g/mol}$

$[NH_4^+] = \dfrac{0.56457\ mol\ NH_4Cl}{0.150L} = 3.764\ M$

$pKa;\ K_b = 1.8 \times 10^{-5},\ pK_b = 4.74,\ pKa + pKb = 14,\ so\ pKa = 9.26$

$pH = 9.26 + \log\left(\dfrac{3.50}{3.764}\right) = \boxed{9.23}$

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 / conjugate 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!

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

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.