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

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$; $K_b = 1.8 \times 10^{-5}$

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, $pH = 14 - 4.74$

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 ($HC_2H_3O_2$) and its conjugate base ($NaC_2H_3O_2$) (as the SALT)
2. Make a mixture of a weak base (NH_3) and its conjugate acid (NH_4Cl) (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 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!

$[NH_3] = ?$; $M_1V_1 = M_2V_2$ $(18.1\ M)(29.0\ mL) = M_2(150.\ mL)$

$M_2 = [NH_3] = 3.50\ M$

$[NH_4^+] = ?$

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

$= 0.56457\ mol\ NH_4Cl$

NH_4Cl: N: 1×14.01; H: 4×1.008; Cl: 1×35.45; $53.492\ g/mol$

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

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

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

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!

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

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.