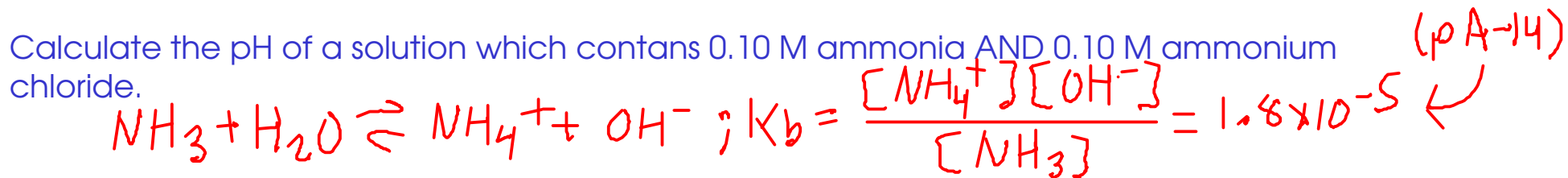


Calculate the pH of a solution which contains 0.10 M ammonia AND 0.10 M ammonium chloride.



As we did with the solution that only contained ammonia initially, set up an equilibrium chart!

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{NH}_4^+$	0.10	+x	0.10 + x
$\text{OH}^-$	0	+x	x
$\text{NH}_3$	0.10	-x	0.10 - x

Let 'x' equal the increase in ammonium ion concentration...

Plug back into equilibrium expression ...

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

If we assume x is much smaller than 0.10, then ...  
 $0.10 - x = 0.10$  AND  
 $0.10 + x = 0.10$

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

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

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

$$\text{pOH} = 4.74, \text{ and}$$

$$\text{pH} = 14.00 - 4.74 = \boxed{9.26}$$

For comparison, pH of 9.26 is still basic, but the pH of the ammonia-only solution is MORE basic (11.13).

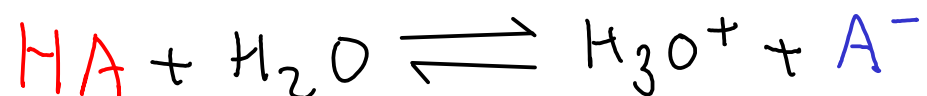
## BUFFERS

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

Made in one of two ways:

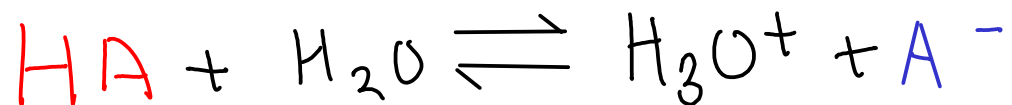
- ① Make a mixture of a weak acid and its conjugate base (as the SALT)  
 $\text{HC}_2\text{H}_3\text{O}_2$                        $\text{NaC}_2\text{H}_3\text{O}_2$
- ② Make a mixture of a weak base and its conjugate acid (as the SALT)  
 $\text{NH}_3$                                        $\text{NH}_4\text{Cl}$

For a weak acid, you would:



- Add HA (weak acid)
- Add a salt containing  $\text{A}^-$  (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.



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

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[A^-]$  ... 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.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

ex: acidic buffer



$$\text{pH} = \text{p}K_{a, \text{HC}_2\text{H}_3\text{O}_2} + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

ex: basic buffer



$$\text{pH} = \text{p}K_{a, \text{NH}_4^+} + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

$$\text{p}K_a + \text{p}K_b = 14,00 \quad \dots \text{ is the } -\log \text{ of } K_a \times K_b = K_w$$

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.

$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[\text{NH}_3]$ : Ammonia was diluted ... use  $M_1V_1 = M_2V_2$

$$(29 \text{ mL})(18.1 \text{ M}) = M_2(150. \text{ mL}) ; M_2 = 3.499333333 \text{ M NH}_3$$

$[\text{NH}_4^+]$ : Dissolved solid ammonium chloride into 150 mL volume. Find moles of solid!

$$30.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}} = 0.5645704031 \text{ mol NH}_4\text{Cl}$$

$$\frac{0.5645704031 \text{ mol NH}_4^+}{0.150 \text{ L}} = 3.763802687 \text{ M NH}_4^+$$

$\text{p}K_a$ :  $K_{a,\text{NH}_4^+} = ?$   $K_{b,\text{NH}_3} = 1.8 \times 10^{-5}$ ;  $\text{p}K_b = 4.74$

Since  $\text{p}K_a + \text{p}K_b = 14$ ,  $\text{p}K_a + 4.74 = 14$ ,  $\text{p}K_a = 9.26$

Use H-H instead of equilibrium chart ...

$$\text{pH} = 9.26 + \log \left( \frac{3.499333333 \text{ M NH}_3}{3.763802687 \text{ M NH}_4^+} \right) = \boxed{9.22}$$