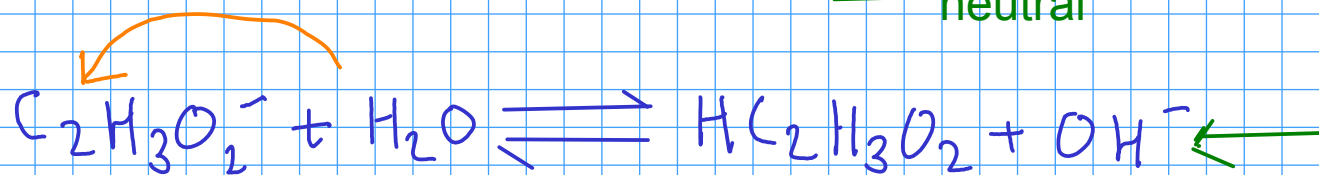


0.100 M $\text{NaC}_2\text{H}_3\text{O}_2$, Find pH



conjugate of acetic acid
 $\text{HC}_2\text{H}_3\text{O}_2$

neutral



Sodium
acetate
is a BASIC
salt

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = ?$$

$$K_a, \text{HC}_2\text{H}_3\text{O}_2 = 1.75 \times 10^{-5}$$

$$K_a \times K_b = K_w \dots \text{true for conjugate pairs}$$

$$(1.75 \times 10^{-5})(K_b) = (1.00 \times 10^{-14})$$

$$K_b = 5.71 \times 10^{-10}$$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.71 \times 10^{-10}$$

	initial	Δ	equilibrium
$[HC_2H_3O_2]$	0	+X	X
$[OH^-]$	0	+X	X
$[C_2H_3O_2^-]$	0.100	-X	0.100 - X

"X" = amount of acetate ion that reacts

$$\frac{X^2}{0.100 - X} = 5.71 \times 10^{-10}$$

↓ $0.100 - X \approx 0.100, X \ll 0.100$

$$\frac{X^2}{0.100} = 5.71 \times 10^{-10}$$

$$X = 7.56 \times 10^{-6} = [OH^-]$$

$$x = 7,56 \times 10^{-6} = [\text{OH}^-]$$

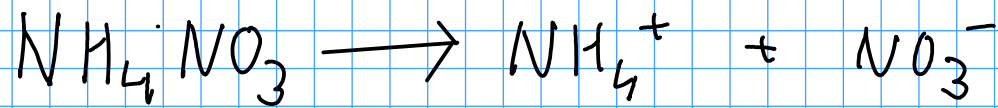
$$\text{pOH} = 5.12 \quad \dots \text{remember, this isn't the answer. We need *pH*!}$$

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 8.88$$

... compare to strong base. 0.100M solution has a pH of 13.00

0.150 M NH_4NO_3 , find pH



NH_4^+ : $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ Ammonia is a weak base, so it's stable in water. Ammonium ion, therefore, is acidic.

NO_3^- : $\text{NO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + \text{OH}^-$ Nitric acid is a STRONG acid, meaning that it completely ionizes in water. So nitrate ion is neutral.

$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$... so we solve the acid equilibrium.

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = ?$$

$$K_b, \text{NH}_3 = 1.8 \times 10^{-5}$$
$$K_a \times K_b = 1.0 \times 10^{-14}$$
$$K_a = 5.56 \times 10^{-10}$$

	I	A	E
$[\text{NH}_3]$	0	+x	x
$[\text{H}_3\text{O}^+]$	0	+x	x
$[\text{NH}_4^+]$	0.150	-x	0.150 - x

$$\frac{x^2}{0.150 - x} = 5.56 \times 10^{-10}$$

$$\frac{x^2}{.150 - x} = 5.56 \times 10^{-10}$$

Assume
 $.150 - x \approx .150$

$$\frac{x^2}{.150} = 5.56 \times 10^{-10}$$

$$x = 9.13 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5.04$$

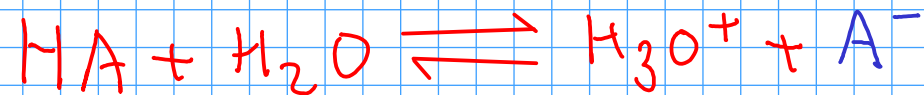
BUFFERS

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

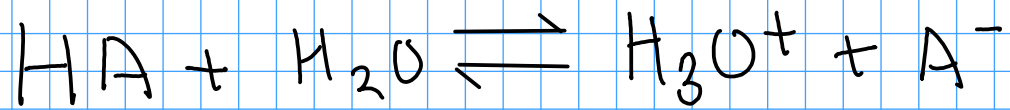
Made in one of two ways:

- 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)
 NH_3 NH_4Cl

For a weak acid, you would:



- 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.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

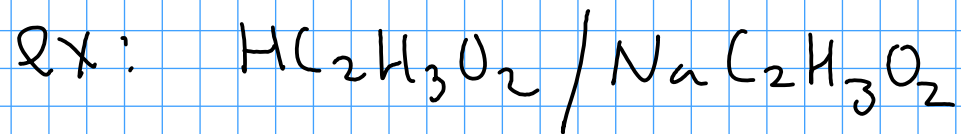
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[\text{A}^-]$... from the salt

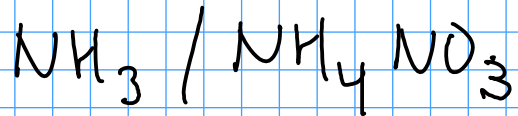
$[\text{HA}]$... from the weak acid

- 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.

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



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



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

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

Calculate the pH of a buffer made from 3.2 grams of ammonium chloride and 29 mL of 18.1 M ammonia diluted to 50.0 mL with water.

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

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

$$3.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} = 0.0598 \text{ mol}$$

$$\frac{0.0598 \text{ mol}}{0.0500 \text{ L}} = 1.196 \text{ M NH}_4^+ \quad \dots \text{ molarity of the ammonium (acid)}$$

$$M_1 V_1 = M_2 V_2$$

$$(18.1 \text{ M})(29 \text{ mL}) = M_2 (50.0 \text{ mL}) \quad M_2 = 10.498 \text{ M NH}_3$$

... molarity of the ammonia (base)

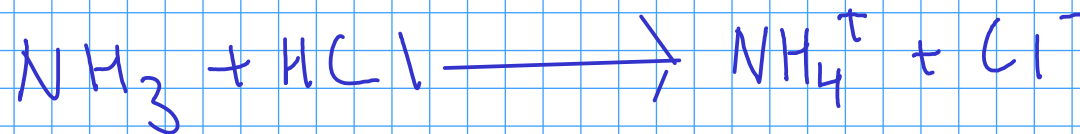
$$\text{p}K_{a, \text{NH}_4^+} = -\log(5.56 \times 10^{-10}) = 9.255$$

$$\text{pH} = \underline{\underline{9.255}} + \log \left(\frac{10.498}{1.196} \right) = \boxed{10.20} \quad \dots \text{ pH of the buffer solution.}$$

BUFFER SELECTION

- Buffer pH is controlled by the pKa of the acidic species in the buffer.
- 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!

Some buffer "recipes" call for making the conjugate ion FROM the weak acid or base ... by adding a STRONG acid or base!



If you have more ammonia than hydrochloric 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!

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

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.