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

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- ; \ k_b = 1.8 \times 10^{-5} \]

<table>
<thead>
<tr>
<th>Species</th>
<th>[Init]</th>
<th>Δ</th>
<th>[Equl]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH4⁺</td>
<td>0.10</td>
<td>+x</td>
<td>0.10+x</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.10</td>
<td>−x</td>
<td>0.10−x</td>
</tr>
</tbody>
</table>

\[
k_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

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

Assume 'x' is small relative to 0.10
0.10 + x ≈ 0.10
0.10 - x ≈ 0.10

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

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

\[
\rho\text{OH} = -\log_{10}(1.8 \times 10^{-5}) = 4.74
\]

So, \[ \rho\text{H} = 14 - 4.74 \]

\[ \rho\text{H} = 9.26 \]

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)
   - $\text{HC}_2\text{H}_3\text{O}_2$  
   - $\text{NaC}_2\text{H}_3\text{O}_2$
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:

$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

- 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.
\[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]

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

1. Take log of both sides
2. Multiply by -1
3. Rearrange, solving for pH

\[ \text{pH} = pK_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right) \]

Henderson-Hasselbalch Equation

\([\text{A}^-]\) ... 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.
\[ \text{pH} = \text{pK}_a,_{\text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \]

**Henderson-Hasselbalch Equation**

**Example: Acidic Buffer**

\[ \text{HC}_2\text{H}_3\text{O}_2 / \text{NaC}_2\text{H}_3\text{O}_2 \]

\[ \text{pH} = \text{pK}_a,_{\text{HC}_2\text{H}_3\text{O}_2} + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right) \]

**Example: Basic Buffer**

\[ \text{NH}_3 / \text{NH}_4\text{NO}_3 \]

\[ \text{pH} = \text{pK}_a,_{\text{NH}_4^+} + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right) \]

\[ \text{pK}_a + \text{pK}_b = 14.00 \ldots \text{is the -log of } K_a \times K_b = K_w \]
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.

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

- Acid: \( NH_4^+ \)
- Base: \( NH_3 \)

\[
NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+
\]

To use the H-H equation, we need to know the concentration of both ammonia (the base) and ammonium ion (the acid) in the buffer!

\[
\frac{M_1 V_1}{M_2 V_2} = \frac{(18.1 \text{M})(29.0 \text{mL})}{150.0 \text{mL}}
\]

\[
M_2 = [NH_3] = 3.50 \text{ M}
\]

\[
[NH_4^+] = ?
\]

\[
30.2 \text{ g} \text{NH}_4 \text{Cl} \times \frac{\text{mol NH}_4 \text{Cl}}{53.492 \text{ g} \text{NH}_4 \text{Cl}} = \frac{0.56457 \text{ mol} \text{NH}_4 \text{Cl}}{0.150 \text{ L}}
\]

\[
[NH_4^+] = \frac{0.56457 \text{ mol} \text{NH}_4 \text{Cl}}{0.150 \text{ L}} = 3.764 \text{ M}
\]

\[
pK_a; \quad K_b = 1.8 \times 10^{-5}, \quad pK_b = 4.74, \quad pK_a + pK_b = 14, \quad pK_a = 9.26
\]

\[
pH = 9.26 + \log \left( \frac{3.50}{3.764} \right) = 9.23
\]
**BUFFER SELECTION**

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

\[ pH = pK_a,_{acidic} + \log \left( \frac{[basic\ species]}{[acidic\ species]} \right) \]

- 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!

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^- \]

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!
- 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!

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

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.