Determine the pH of a solution that is 0.20 M NH$_3$ and 0.30 M NH$_4$Cl.

Consider mixture of salt NaA and weak acid HA.

NaA (aq) $\rightleftharpoons$ Na$^+$ (aq) + A$^-$ (aq)

HA (aq) $\rightleftharpoons$ H$^+$ (aq) + A$^-$ (aq)

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

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

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

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

$pH = pK_a + \log \frac{[A]}{[HA]}$

$pK_a = -\log K_a$

What is the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK?

Mixture of weak acid and conjugate base:

HCOOH (aq) $\rightleftharpoons$ H$^+$ (aq) + HCOO$^-$ (aq)

Initial (M) 0.30 0.00 0.52
Change (M) -x +x +x
Equilibrium (M) 0.30 - x x 0.52 + x

Common ion effect

$\text{pH} = pK_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$

$0.30 - x = 0.30$

$0.52 + x = 0.52$

$pH = 3.77 + \log \frac{0.52}{0.30} = 4.01$

HCOOH $pK_a = 3.77$

$K_w = 1.7 \times 10^{-5}$

A buffer solution is a solution of:
1. A weak acid or a weak base and
2. The salt of the weak acid or weak base

Both must be present!

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

Consider an equal molar mixture of CH$_3$COOH and CH$_3$COONa:

Add strong acid

H$^+$ (aq) + CH$_3$COO$^-$ (aq) $\rightarrow$ CH$_3$COOH (aq)

Add strong base

OH$^-$ (aq) + CH$_3$COOH (aq) $\rightarrow$ CH$_3$COO$^-$ (aq) + H$_2$O (l)
Calculate the pH of the 0.20 M NH$_3$/0.24 M NH$_4$Cl buffer.

What is the pH of the buffer after the addition of 10.0 mL of 0.10 M HCl to 62.5 mL of the buffer?

Calculate the pH of the 0.30 M NH$_3$/0.36 M NH$_4$Cl buffer solution. What is the pH after the addition of 20.0 mL of 0.050 M NaOH to 80.0 mL of the buffer solution?

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

\[\text{p}K_a = 9.25 \quad \text{pH} = 9.25 + \log \left( \frac{0.30}{0.36} \right) = 9.17 \]

Start (moles) \begin{align*}
\text{NH}_4^+ (aq) & \quad \text{H}^+ (aq) + \text{NH}_3 (aq) \\
0.29 & \quad 0.011 \quad 0.24
\end{align*}

End (moles) \begin{align*}
\text{NH}_4^+ (aq) & \quad \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) + \text{NH}_3 (aq) \\
0.028 & \quad 0.0 \\
0.025 & \quad 0.025
\end{align*}

Final volume = 80.0 mL + 20.0 mL = 100 mL

\[
\frac{[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{0.028}{0.10} \quad \text{pH} = 9.25 + \log \left( \frac{0.25}{0.28} \right) = 9.20
\]

Titrations

In a titration a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

**Equivalence point** – the point at which the reaction is complete

**Indicator** – substance that changes color at (or near) the equivalence point

Slowly add base to unknown acid UNTIL

The indicator changes color (pink)

**Strong Acid-Strong Base Titrations**

\[
\text{NaOH (aq)} + \text{HCl (aq)} \rightarrow \text{H}_2\text{O} (l) + \text{NaCl (aq)}
\]

\[
\text{OH}^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{O} (l)
\]

\[
\text{pH} = 7
\]

Volume of NaOH added (mL) 10

4.7
**Weak Acid-Strong Base Titrations**

\[ \text{CH}_3\text{COOH} (aq) + \text{NaOH} (aq) \rightarrow \text{CH}_3\text{COONa} (aq) + \text{H}_2\text{O} (l) \]
\[ \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O} (l) \]

At equivalence point (pH > 7):
\[ \text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{OH}^- (aq) + \text{CH}_3\text{COOH} (aq) \]

**Strong Acid-Weak Base Titrations**

\[ \text{HCl} (aq) + \text{NH}_3 (aq) \rightarrow \text{NH}_4\text{Cl} (aq) \]
\[ \text{H}^+ (aq) + \text{NH}_3 (aq) \rightarrow \text{NH}_4^+ (aq) + \text{H}^+ (aq) \]

At equivalence point (pH < 7):
\[ \text{NH}_4^+ (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{NH}_3 (aq) + \text{H}_3\text{O}^+ (aq) \]

**Exact 100 mL of 0.10 M HNO_2 are titrated with a 0.10 M NaOH solution. What is the pH at the equivalence point?**

**Start (moles):**
- HNO_2 (aq) + OH^- (aq) → NO_2^- (aq) + H_2O (l)
- 0.01

**End (moles):**
- 0.01
- 0.01
- NO_2^- (aq) + H_2O (l) → OH^- (aq) + HNO_2 (aq)
- 0.01

**Final volume = 200 mL**

\[ [\text{NO}_2^-] = \frac{0.01}{0.200} = 0.05 \text{ M} \]

\[ K_b = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{x^2}{0.05-x} = 2.2 \times 10^{-11} \]

\[ x = 1.05 \times 10^{-6} \]

\[ [\text{OH}^-] = 14 - pOH = 8.02 \]

**Acid-Base Indicators**

\[ [\text{HIn}] \geq 10 \]

Color of acid (HIn) predominates

\[ [\text{HIn}] \leq 10 \]

Color of conjugate base (In^-) predominates

**Some Common Acid-Base Indicators**

**Which indicator(s) would you use for a titration of HNO_2 with KOH?**

Weak acid titrated with strong base.

At equivalence point, will have conjugate base of weak acid.

At equivalence point, pH > 7

Use cresol red or phenolphthalein