WEAK ACIDS AND BASES

[MH5; Chapter 13]

• Recall that a strong acid or base is one which completely ionizes in water............

\[
\text{HCl} \quad \overset{\text{H}_2\text{O}}{\rightarrow} \quad \text{H}^+ \quad + \quad \text{Cl}^- \quad \text{Acidic}
\]

\[
\text{NaOH} \quad \overset{\text{H}_2\text{O}}{\rightarrow} \quad \text{Na}^+ \quad + \quad \text{OH}^- \quad \text{Basic}
\]

• In contrast a weak acid or base is only partially ionized in aqueous solution....................

\[
\text{Weak acid} : \quad \text{HA} \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{A}^-
\]

\[
\text{Weak base} : \quad \text{B} + \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{BH}^+ \quad + \quad \text{OH}^-
\]

• The ionization of a weak acid or base in water is an equilibrium situation.

• It is, therefore, governed by an equilibrium constant; \(K_a\) for acids and \(K_b\) for bases.

• We write these equilibrium constants as:

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

\[
K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}
\]
Notice that....

- \([H_2O]\) (constant at \(\approx 55.6\ M\)) does not appear in \(K_a\) or \(K_b\).
- The larger the \(K_a\) the stronger the acid; the larger the \(K_b\) the stronger the base.

**EXAMPLE:**

\(CCl_3COOH; \quad K_a = 2.0 \times 10^{-1}\) is a stronger acid than
\(CH_3COOH; \quad K_a = 1.8 \times 10^{-5}\)

\(CH_3NH_2; \quad K_b = 6.4 \times 10^{-4}\) is a stronger base than
\(NH_3; \quad K_b = 1.8 \times 10^{-5}\)

- H’s on C are not (generally) acidic in water - e.g. \(\text{CH}_3\text{COOH}\) monoprotic (one H\(^+\)) and one \(K_a\)
- We may define \(pK_a\) analogous to \(pH\) and \(pK_w\):

\[
pK_a = - \log K_a \quad \quad \quad \quad \quad \quad \quad \quad pK_b = - \log K_b
\]

**EXAMPLES:**

\(pK_a\) for \(CCl_3COOH = 0.70\) \(\quad [ - \log (2.0 \times 10^{-1})]\)
\(pK_a\) for \(CH_3COOH = 4.74\) \(\quad [ - \log (1.8 \times 10^{-5})]\)

\(pK_b\) for \(CH_3NMNH_2 = 3.19\) \(\quad [ - \log (6.4 \times 10^{-4})]\)
\(pK_b\) for \(NH_3 = 4.74\) \(\quad [ - \log (1.8 \times 10^{-5})]\)

- Because of the minus sign, the smaller the value of \(K_a\) or \(K_b\) the larger the value of \(pK_a\), or \(pK_b\)

\[
\begin{align*}
\text{OR} \\
\text{The weaker the acid or base, the larger the } pK_a \text{ or } pK_b \\
\end{align*}
\]
Calculations Involving Weak Acids

• Suppose that we have a solution of acetic acid, \( CH_3COOH \) (\( K_a = 1.8 \times 10^{-5} \)); let its initial concentration be represented by “c” mol L\(^{-1} \). At equilibrium, “x” mol L\(^{-1} \) have dissociated.

\[
\begin{align*}
CH_3COOH & \rightarrow H^+ + CH_3COO^-\\
By: & \quad c \\
EQ: & \quad c - x \\ 
K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} & = \frac{(x)(x)}{c-x} = \frac{x^2}{c-x}
\end{align*}
\]

• This is a quadratic equation in “x”. \((ax^2 + bx + c = 0)\)

• The quadratic equation may be simplified by assuming that “x” is negligible compared to “c”.

• \( CH_3COOH \) is a weak acid; so we may assume that the small amount dissociation makes little difference to the amount of undissociated acid left.

• Now let “c” = 0.10 mol L\(^{-1} \). So… \( c - x \approx c \)

\[
K_a = \frac{x^2}{0.10 - x} = 1.8 \times 10^{-5}
\]
• If \( x \) is negligible compared to 0.10 molL\(^{-1}\):

\[
\Rightarrow 0.10 - x \approx 0.10
\]

So...

\[
1.8 \times 10^{-5} = \frac{x^2}{0.10}
\]

\[
x^2 = 1.8 \times 10^{-5} \times 0.10
\]

\[
x = \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.34 \times 10^{-3} = [H^+]
\]

• In this case, \( x \) is about 1.3% of 0.10, a negligible error within the accuracy of the original data we were given.

• If we were to solve the equation exactly, \( x = 1.333 \times 10^{-3} \) M, so the approximate answer \( 1.342 \times 10^{-3} \) M only differs from the exact answer by \( 0.009 \times 10^{-3} \), an "error" of less than 1%.

**General Guideline:**

• This assumption; a 'negligible' amount of the acid being ionized - is acceptable if \( x \leq 5\% \) of the initial concentration of acid......

• This will generally be the case if the concentration of the acid, \( c \), divided by the \( K_a \) value is \( > 100 \).

**EXAMPLE:** \([\text{CH}_3\text{COOH}] = 0.10 \text{ M} ; \ K_a = 1.8 \times 10^{-5}\)

Test the assumption that \( c - x \approx c \):

\[
\frac{c}{K_a} \quad \text{must be greater than} \quad 100
\]

\[
\Rightarrow \frac{0.10}{1.8 \times 10^{-5}} = 5555 \quad \therefore \text{"assumption" \ is valid}
\]
• The quantity $\frac{[x / c]}{x} \times 100$ is called the degree of dissociation, expressed on a % basis; may also be called percent dissociation or ionization.

$$\text{Percent dissociation} = \frac{\text{Amount dissociated}}{\text{Original amount}} \times 100\%$$

$$= \frac{x}{c} \times 100$$

From example: $\%$ ionization $= \frac{1.34 \times 10^{-3}}{0.10} \times 100$

$= 1.34\%$

• We can also use $x$ to calculate pH; because in a weak acid equilibrium; $x = [H^+]$

$[H^+] = 1.34 \times 10^{-3} \text{ M}$, therefore $\text{pH} = 2.87$

• The degree of dissociation increases as the solution is diluted, although $[H^+]$ decreases.

**EXAMPLE:** For solutions of HF in water:

$K_a$ for HF $= 6.7 \times 10^{-4}$

<table>
<thead>
<tr>
<th>Initial HF</th>
<th>Equil. $[H^+]$</th>
<th>% Dissoc.</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>$2.6 \times 10^{-2}$</td>
<td>2.6</td>
<td>1.59</td>
</tr>
<tr>
<td>0.1</td>
<td>$7.9 \times 10^{-3}$</td>
<td>7.9</td>
<td>2.10</td>
</tr>
<tr>
<td>0.01</td>
<td>$2.3 \times 10^{-3}$</td>
<td>22</td>
<td>2.64</td>
</tr>
</tbody>
</table>

decreasing  increasing  increasing
• What if we need to do the exact calculation?
• We have to solve the quadratic:
  \[ a \chi^2 + b \chi + c = 0 \]
  \[ \chi^2 + K_a \chi - K_a C = 0 \]
  (from expansion of \( K_a = x^2/(C - x) \))
  
  \[ 1.8 \times 10^{-5} = \frac{x^2}{0.100 - x} \]
  
  \[ x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0 \]
  
  \[ \chi = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]
  
  \[ \chi = 1.333 \times 10^{-3} \]

• What else can we calculate using \( K_a \)?
• The \( K_a \) expression says:
  \[ HA \rightleftharpoons H^+ + A^- \]
  
  \[ K_a = \frac{[H^+] [A^-]}{[HA]} \]

• Depending on the information given, we could also calculate the initial concentration of the weak acid or the actual value of \( K_a \)...........

**Strategy**

• Always write the reaction for the weak acid given in the question.
• Write the equilibrium constant expression for the reaction.
• Identify what you know and what you are asked to find.
• Usually, it’s a fairly straightforward matter of substituting for the appropriate variables in the Equilibrium Constant Expression.
• Sometimes there are a few intermediate calculations to perform....
EXAMPLE 1:
Nitrous acid, HNO₂ has a \( K_a \) value of \( 6.0 \times 10^{-4} \).
Calculate the initial concentration of HNO₂ if a solution of this acid has a pH of 3.65.

\[
\text{By: } \frac{C}{0} = \frac{H^+ + NO_2^-}{C}
\]

\[
\text{Eq: } C - x \quad x \quad x
\]

\[
K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{C - x}
\]

\[
\text{pH} = 3.65 = [H^+] = 10^{-3.65}
\]

\[
= 2.238 \times 10^{-4}
\]

\[
= x
\]

Substituting:

\[
6.0 \times 10^{-4} = \left(\frac{2.238 \times 10^{-4}}{C - 2.238 \times 10^{-4}}\right)^2
\]

\[
C - 2.238 \times 10^{-4} = \left(2.238 \times 10^{-4}\right)^2 \frac{1}{6.0 \times 10^{-4}}
\]

\[
\therefore C = \left(2.238 \times 10^{-4}\right)^2 + 2.238 \times 10^{-4} = 3.1 \times 10^{-4} \text{ M}
\]
EXAMPLE 2:  

A 0.025 M solution of formic acid, HCOOH, has a pH of 2.75.

a) Calculate the % ionization of this solution.
b) Calculate the \( K_a \) for formic acid.

\[
\text{Eq: } \quad \text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^- \\
\text{By: } \quad 0.025 \quad 0 \quad 0 \\
\text{Eq: } \quad 0.025 - x \quad x \quad x
\]

\[
\text{pH} = 2.75 \implies [\text{H}^+] = 10^{-2.75} = 1.78 \times 10^{-3} \, \text{mol L}^{-1}
\]

\[a) \quad \% \text{ ionization} = \frac{x}{C} \times 100 \]
\[= \frac{1.78 \times 10^{-3}}{0.025} \times 100 \]
\[= 7.12\% \]

\[b) \quad K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{C - x} \quad \text{(Don't neglect } x \text{ when known)}
\]
\[= \frac{(1.78 \times 10^{-3})^2}{0.025 - 1.78 \times 10^{-3}}
\]
\[= 1.36 \times 10^{-4} \]
**Calculations Involving Weak Bases**

- The most commonly used weak bases are Ammonia ($NH_3$) and its derivatives.
- In these compounds one (or more) N atom has a pair of electrons not used (yet!) for bonding (a "lone pair").

**EXAMPLES:**

\[
NH_3 + H_2O \rightarrow NH_4^+ + OH^-
\]

\[
CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-
\]

- We may write $K_b$ expressions for both of these......

\[
K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}\

K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}\

- Problems using $K_b$ are treated in the same manner as problems using $K_a$ (weak acid).
EXAMPLE 1:
What is the % ionization and pH of a solution of a 0.085 M solution of
NH₃? \([K_b = 1.8 \times 10^{-5}]\)

\[
\begin{align*}
NH_3 + H_2O & \rightleftharpoons NH_4^+ + OH^- \\
\text{By:} & \quad 0.085 \\
\text{Eq:} & \quad 0.085 - \chi
\end{align*}
\]

\[
K_b = \frac{\chi^2}{0.085 - \chi}
\]

\[
1.8 \times 10^{-5} = \frac{\chi^2}{0.085}
\]

\[
\chi = \sqrt{1.8 \times 10^{-5} \times 0.085}
\]

\[
= 1.24 \times 10^{-3} = [OH^-]
\]

\[
\Rightarrow \rho_{OH} = 2.91 \quad \Rightarrow \rho_H = 14 - 2.91 = 11.09
\]

% Ionization = \[
\frac{\chi}{C} \times 100
\]

\[
= \frac{1.24 \times 10^{-3}}{0.085} \times 100
\]

\[
= 1.46\%
\]
EXAMPLE 2:
A solution of methylamine, \( CH_3NH_2 \), has a pH of 10.45. Calculate the initial concentration of methylamine in this solution.

\([K_b \text{ of } CH_3NH_2 = 6.4 \times 10^{-4}]\)

\[
\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-
\]

By:
\[
\text{C} - x
\]

Eq:
\[
\text{C} - \text{x}
\]

\(\text{pH} = 10.45\); \(\text{pH} > 7\) : Basic Soln

\(\therefore \text{pOH} = 3.55\) \(\Rightarrow [\text{OH}^-] = 10^{-3.55}\)

\(= 2.83 \times 10^{-4}\) mol/L

\(K_b = \frac{x^2}{C - x}\)

\(6.4 \times 10^{-4} = \left(2.82 \times 10^{-4}\right)^2\)

\(\frac{C}{C - 2.82 \times 10^{-4}}\)

\(C = 4.06 \times 10^{-4}\) mol/L\(^{-1}\)
EXAMPLE 3:
Calculate the $K_b$ for the weak base $B$, if a 0.00365 M solution of that base is 8.50 % ionized.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Ref: 0.00365 0 0
Eq: 0.00365 -x x x

\[
\text{% ionization} = \frac{x}{c} \times 100
\]

\[
\Rightarrow \frac{x}{0.00365} \times 100 = 8.50\%
\]

\[
\frac{x}{0.00365} = 0.0850
\]

\[
\therefore x = 3.102 \times 10^{-4} = [OH^-]
\]

\[
K_b = \frac{x^2}{c-x} = \frac{(3.102 \times 10^{-4})^2}{0.00365 - 3.102 \times 10^{-4}}
\]

\[
= 2.88 \times 10^{-5}
\]
Reactions of Conjugate Species

- Every weak acid (HA), will produce its **conjugate base** (A\(^-\)) when it ionizes in water.

\[
HA + H_2O \rightleftharpoons H_3O^+ + A^- \\
\text{or}
HA \rightleftharpoons H^+ + A^- 
\]

- The conjugate base of any acid is the species that is obtained from the acid by removal of one H\(^+\) (or proton).

\[- A^- \text{; came from } HA \]

- Every weak base (B), will produce its **conjugate acid** (BH\(^+\)) when it ionizes in water.

\[
B + H_2O \rightleftharpoons BH^+ + OH^- 
\]

- Similarly, the conjugate acid of any base is the species that is obtained from the base by addition of a proton (or H\(^+\)).

\[- BH^+ \text{; came from } B \]

- It is essential to realize that in any conjugate acid/base pair, the acid always has one more H than the base!
- You must be able to recognize conjugate bases and acids, based on the original weak acid or base!

\[
\begin{align*}
HA / A^- & \quad \text{acid / base} \\
B / BH^+ & \quad \text{base / acid}
\end{align*}
\]
EXAMPLES:
- Consider the weak acid HNO₂; its conjugate base is NO₂⁻.
- Now look at the weak base NH₃; its conjugate acid is NH₄⁺.
- HNO₂ / NO₂⁻ and NH₃ / NH₄⁺ are conjugate acid-conjugate base pairs [differing by one H⁺]
- How do these conjugate species behave?
- What happens if you react them with water?
- Consider the generic weak acid, HA; its conjugate base is A⁻.
- This species will act as a base: Base take H⁺ from H₂O

\[
A^- + H_2O \rightleftharpoons HA + OH^- \quad \text{Base soln}
\]

- This reaction is often called hydrolysis.
- What is \( K_b \) for A⁻, and how is it related to \( K_a \) for HA?

\[
\text{For } A^-: \quad A^- + H_2O \rightleftharpoons HA + OH^- \quad K_b = \frac{[HA][OH^-]}{[A^-]}
\]

\[
\text{For } HA: \quad HA \rightleftharpoons H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]}
\]

Adding: \( H_2O \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] \)

- Or...to get the same result, we could add the equations, and then (as we have seen earlier in these notes; p. 137) their K’s are multiplied:

\[
K_w = K_a \times K_b \quad -\text{for ANY conj acid/base pr.}
\]

\[
K_b (A^-) = \frac{K_w}{K_a (HA)}
\]
• The relationship \( K_a \times K_b = K_w \) is always true for a conjugate acid-base pair.
• The **weaker** the acid, the more **basic** is its conjugate base.

We can also use the log scale........................

\[
pK_a + pK_b = pK_w = 14.0
\]

**EXAMPLE 1:**
HF, a weak acid: \( K_a = 7.24 \times 10^{-4}; \) \( pK_a = 3.14 \)
F\(^-\), (conjugate base of HF)
\[pK_b = 14.00 - 3.14 = 10.86\]
\[K_b = 1.38 \times 10^{-11}\]  \(\text{very weak base}\)

**EXAMPLE 2:**
CH\(_3\)COOH, a weak acid: \( K_a = 1.8 \times 10^{-5}; \) \( pK_a = 4.74 \)
CH\(_3\)COO\(^-\), (conjugate base of CH\(_3\)COOH)
\[pK_b = 14.00 - 4.74 = 9.26\]
\[K_b = 5.56 \times 10^{-10}\]  \[
\frac{K_b}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}
\]

**EXAMPLE 3:**
HCN, a very weak acid: \( K_a = 4.00 \times 10^{-10}; \) \( pK_a = 9.40 \)
CN\(^-\), (conjugate base of HCN)
\[pK_b = 14.00 - 9.40 = 4.60\]
\[K_b = 2.5 \times 10^{-5}\]  \(\text{a stronger weak base}\)
Now look at the generic weak base B, whose conjugate acid is BH⁺.

BH⁺ will act like an acid......

\[
BH^+ \rightleftharpoons B + H^+
\]

We also call this a hydrolysis reaction.

We can determine \( K_a \) for this conjugate acid in the same manner as we determined \( K_b \) for a conjugate base previously............

\[
K_b = \frac{[BH^+][OH^-]}{[B]}
\]

\[
K_a = \frac{[BH^+][H^+]}{[B]}
\]

\[
K_b \times K_a = K_w
\]

As was the case with the weak acids, the **weaker** the base, the more acidic is its conjugate acid.

**EXAMPLE 1:**

NH₃ is a weak base; \( K_b = 1.8 \times 10^{-5} \); pKₐ = 4.74

NH₄⁺ (conjugate acid of NH₃): \( pK_a = 14.00 - 4.74 = 9.26 \)

\( K_a (NH_4^+) = 5.56 \times 10^{-10} \) Very weak acid.

**EXAMPLE 2:**

Aniline, C₆H₅NH₂, is a very weak base; \( K_b = 4.0 \times 10^{-10} \); pKₐ = 9.40

C₆H₅NH₃⁺ (conjugate acid of C₆H₅NH₂): \( pK_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5} \)

- Stronger weak acid
Salts

- You may have noticed that the conjugate base of a weak acid, or the conjugate acid of a weak base is always an ion.
- So where does this ion come from?
- It is always produced when the “parent” weak acid or base ionizes, but these conjugate species can be also be found in ionic compounds.
- And ions are formed when an ionic solid is dissolved in water.
- Remember those solubility rules?
- This is where they come in handy; so you will know whether or not a solid will dissolve in water to produce ions!!

First we consider salts that yield the conjugate base of a weak acid.

- Recall that the conjugate base will always behave like a base when in aqueous solution:
  \[B + H_2O \rightleftharpoons BH^+ + OH^-\]

**EXAMPLE 1:**

Consider the salt \(\text{CH}_3\text{COONa}\). In water...........

The \(\text{CH}_3\text{COO}^-\) will now undergoes hydrolysis with water.............

\[\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+\]

\(K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}\)

- The ion that is the conjugate species of a weak acid or base is the species that will undergo the hydrolysis with water.
- Remember that a conjugate species differs from its “parent” species by only one \(H^+\)!!
EXAMPLE 2:
Calculate the pH and % hydrolysis ( % base ionization) in 0.100 M KF.

$\text{[K}_a\text{ for HF} = 7.24 \times 10^{-4}]$

\[ \text{HF} \rightarrow \text{K}^+ + \text{F}^- \quad \therefore \quad [\text{F}^-] = 0.100 \text{M} \]

- Look at F$^-$: one less H than HF
  \[ \therefore \text{F}^- \text{ is a conjugate of HF} \]
- HF is a weak acid (because we know $\text{K}_a$)
  \[ \therefore \text{F}^- \text{ is the conjugate base of HF} \]

\[ \text{Eq}: \text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^- \]

By! 0.100

\[ \text{Eq}: 0.100 - x \]

\[ \begin{align*}
\text{K}_b (\text{F}^-) &= \frac{\text{K}_w}{\text{K}_a (\text{HF})} = \frac{1.0 \times 10^{-14}}{7.24 \times 10^{-4}} = 1.38 \times 10^{-11} \\
\text{K}_b &= \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{x^2}{0.100 - x} \quad - \text{neglect } x
\end{align*} \]

\[ \therefore 1.38 \times 10^{-11} = \frac{x^2}{0.100} \quad \Rightarrow \quad x = \sqrt{1.38 \times 10^{-11} \times 0.100} = 1.17 \times 10^{-6} = [\text{OH}^-] \]

\[ \text{pOH} = 5.93 \quad \Rightarrow \quad \text{pH} = 14 - 5.93 = 8.07 \]

\% Ionization = \[ \frac{x}{c} \times 100 = \frac{1.17 \times 10^{-6}}{0.100} \times 100 \]

\[ = 1.17 \times 10^{-3} \% \]
EXAMPLE 2:
A 0.0285M solution of the sodium salt, NaA of the weak monoprotic acid, HA, has a pH of 9.65. Calculate $K_a$ for the acid, HA.

\[ \text{pH} = 9.65 \quad \Rightarrow \quad \text{pOH} = 4.35 \]

\[ [\text{OH}^-] = 10^{-4.35} = 4.47 \times 10^{-5} = \chi \]

$\text{NaA} \rightarrow \text{Na}^+ + A^- \quad \therefore [A^-] = 0.0285 \text{M}$

If HA is a weak acid, then $A^-$ must be conjugate

\[ \text{eq: } A^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \]

By: $0.0285$

ed: $0.0285 - \chi$

\[ K_b (\text{for A}^-) = \frac{[\text{HA}][\text{OH}^-]}{[A^-]} = \frac{\chi^2}{0.0285 - \chi} \]

\[ = \frac{(4.47 \times 10^{-5})^2}{0.0285 - 4.47 \times 10^{-5}} \]

\[ = 7.00 \times 10^{-8} \]

\[ K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{7.00 \times 10^{-8}} \]

\[ K_a (\text{for HA}) = 1.43 \times 10^{-7} \]
• Salts that produce the conjugate acids of weak bases will exhibit **acidic** behaviour in solution..............

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

**EXAMPLE 1:**

The salt in question is \( \text{NH}_4\text{Cl} \). In water:

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]

The \( \text{NH}_4^+ \) is the conjugate acid of \( \text{NH}_3 \), so in water...

\[ \text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+ \quad \text{\( K_a \) (\text{NH}_4^+)} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \]

**EXAMPLE 2:** Calculate the pH of a solution of 0.175 M \( \text{NH}_4\text{NO}_3 \).

In water:

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

Then.....

\[ \text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3 \]

\[ \text{By: } 0.175 \quad 0 \quad 0 \]

\[ \text{EQ: } 0.175 - \chi \quad \chi \quad \chi \]

\[ \text{\( K_a \) (for \( \text{NH}_4^+ \))} = \frac{\text{\( K_w \)}}{\text{\( K_b \) (for \( \text{NH}_3 \))}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \]

\[ \text{\( K_a = \frac{\chi^2}{0.175 - \chi} \implies 5.56 \times 10^{-10} = \frac{\chi^2}{0.175 - \chi} \)} \]

\[ \chi = \sqrt{5.56 \times 10^{-10} \times 0.175} = 9.86 \times 10^{-6} = [\text{H}^+] \]

\[ \therefore \text{pH} = 5.00 \]
Equivalence Point of a Titration

- This is the point where the stoichiometric quantities of acid and base, defined by the equation, have been mixed.
- It is really important to note that the solution is NOT always neutral (i.e. pH = 7) at the equivalence point !!
- This is why, earlier, we used the term equivalence point rather than neutralization point.
- The pH at the equivalence point is only truly neutral (pH = 7) for a titration of a strong acid with a strong base.

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}
\]

strong \quad \text{neutral}

- So why is the solution of NaCl neutral?
- Because neither Na\(^+\) nor Cl\(^-\) is the conjugate of a weak species (base or acid).....
- If both ions which form the salt (NaCl in this case) originally came from strong species, they may termed spectator ions and the solution will be neutral.

In contrast:

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}
\]

weak \quad \text{basic solution}

- The salt formed in the reaction is \text{CH}_3\text{COO}^- \text{Na}^+.
- The \text{CH}_3\text{COO}^- is a base ; the conjugate base of the weak acid \text{CH}_3\text{COOH}.
- That means that this solution will be basic.
\[
\begin{align*}
\text{HCl} + \text{NH}_3 & \rightarrow \text{NH}_4^+\text{Cl}^- + \text{H}_2\text{O} \\
\text{strong} & \quad \text{weak} & \quad \text{acidic solution} \\
\text{H}^+ + \text{NH}_3 & \rightarrow \text{NH}_4^+
\end{align*}
\]

- The salt formed in this reaction is \( \text{NH}_4^+\text{Cl}^- \).
- The \( \text{NH}_4^+ \) is an acid; the conjugate acid of the weak base \( \text{NH}_3 \).
- So this solution will be acidic.

- There is one other possible combination; that of a weak acid + a weak base: acidic or basic at equivalence depending upon the relative strengths of the acid and base involved..... Ignore!

- What is really happening at the equivalence point in titrations of a weak species with a strong species?

1) \( \text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O} \)
2) \( \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+\text{Cl}^- + \text{H}_2\text{O} \)

- Because one of the species involved in the titration - \( \text{CH}_3\text{COOH} \) in (1) and \( \text{NH}_3 \) in (2) - is a weak species, the reactions are not quite complete (because the weak species never completely ionize.)
- They are, however, close enough to complete that we can assume that the salt is by far the major species at equilibrium.
- So... as a first approximation, we start our calculation by assuming complete reaction to the salt. [As shown by equations 1) & 2).]
- To correct this not-quite-true first approximation, we correct it by allowing a back reaction; this is hydrolysis of water by the salt.

3) \( \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \)
4) \( \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \)

- These hydrolysis reactions are actually the ionic equations corresponding to the reverse of (1) and (2)!!
• How do we put all this information together to solve an equivalence point problem?

• The steps are:

1) Write an equation for the acid base reaction. (Similar to equations 1) or 2) on the previous page.)

2) Determine the number of moles of the acid and base......recall that at the equivalence point, these will be equal.

3) Determine the number of moles of salt formed (equal to the number of moles of acid or base).

4) Determine the total volume of the solution, and the Molarity of the salt solution.

5) Now write an equation for the hydrolysis reaction by the salt. (Similar to equations 3) and 4) on the previous page.)

6) Using $K_w$, calculate $K_a$ or $K_b$ for the salt.

7) Now calculate the concentration of either the $H_3O^+$ or the $OH^-$ formed as a result of hydrolysis.

8) Finally, calculate the pH.
EXAMPLE 1:
Calculate the pH at the equivalence point of the titration of 25.00 mL of 0.165 M benzoic acid, C₆H₅COOH, with 0.185 M KOH. [KOH \rightarrow \text{K}^+ + \text{OH}^-]

\[K_a \text{ for } C_6H_5COOH = 6.6 \times 10^{-5}\]

1. **Rxn:**  \(C_6H_5COOH + \text{OH}^- \rightarrow H_2O + C_6H_5COO^-\)

2. **mol C₆H₅COOH = 0.165 M \times 0.025L = 0.004125 mol**
   
   = mol \(H^+\) reacted = mol \(OH^-\) used
   
   = mol \(C_6H_5COO^-\) formed

3. **Vol KOH = \(\frac{0.004125 \text{ mol}}{0.185 \text{ M}} = 0.02230 \text{ L}\)**

   \([C_6H_5COO^-] = \frac{0.004125 \text{ mol}}{(0.025 + 0.02230) \text{ L}} = 0.0872 \text{ M}\)

4. **EQ:**  \(C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-\)
   
   By: 0.0872
   
   EQ: 0.0872 - \(x\)

5. **\(K_b (\text{for } C_6H_5COO^-) = \frac{K_w}{K_a (\text{for } C_6H_5COOH)} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-5}} = 1.51 \times 10^{-10}\)**

6. **\(K_b = \frac{x^2}{0.0872 - x} \Rightarrow 1.51 \times 10^{-10} = \frac{x^2}{0.0872}\)**
   
   \(x = \sqrt{1.51 \times 10^{-10} \times 0.0872} = 3.63 \times 10^{-6}\)

7. **\([OH^-] = 3.63 \times 10^{-6}\)**

8. **\(pOH = 5.44 \quad \text{pH} = 8.56\)**
EXAMPLE 2:
Calculate the pH at the equivalence point of the titration of 0.175 M methylamine, CH₃NH₂, with 0.250 M HNO₃.

\[ [K_b \text{ for } CH₃NH₂ = 6.4 \times 10^{-4}] \]

\[ \text{We have} \]
\[ \text{Pick a volume for one species; calculate the volume of the other.} \]

\[ \text{Assume 50.0 mL of } CH₃NH₂ \]
\[ \therefore \text{mol } CH₃NH₂ = 0.175 \text{ M} \times 0.050 \text{ L} = 0.00875 \text{ mol} \]

\[ \text{At } EQ \text{ Pt: } \text{mol } CH₃NH₂ = \text{mol } H^+ = 0.00875 \text{ mol} \]
\[ \text{Vol } HNO₃ = \frac{0.00875 \text{ mol}}{0.250 \text{ M}} = 0.035 \text{ L} \]

\[ \text{Rxn: } CH₃NH₂ + H^+ \rightarrow CH₃NH₃^+ \]
\[ [CH₃NH₃^+] = \frac{0.00875 \text{ mol}}{(0.05 + 0.035) \text{ L}} = 0.1029 \text{ M} \]

\[ \text{CH₃NH₃}^+ \text{ is the conjugate acid of } CH₃NH₂ \]

\[ EQ: \quad CH₃NH₃^+ \rightleftharpoons H^+ + CH₃NH₂ \]
\[ 0.1029 \quad 0 \]
\[ 0.1029 - x \quad x \quad x \]

\[ K_a (CH₃NH₃^+) = \frac{K_w}{K_b (CH₃NH₂)} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-11}} = 1.56 \times 10^{-11} \]

\[ 1.56 \times 10^{-11} = \frac{x^2}{0.1029 - x} \]

\[ x = \sqrt{1.56 \times 10^{-11} \times 0.1029} = 1.266 \times 10^{-6} = [H^+] \]

\[ \therefore \text{pH} = 5.90 \]
**Acid Base Indicators** [MH5; 14.2]

- Indicators are used to detect the equivalence point of a titration.
- An indicator is a weak organic acid that has the particular property of being a noticeably different colour from its conjugate base.
- The indicator used must change colour at a pH that closely matches the pH expected at the equivalence point of the titration.
- Over the small pH range where the acid changes over to the conjugate base, we see a change of colour........

\[
HIn \rightarrow H^+ + In^- \quad K_{in} = \frac{[H^+][In^-]}{[HIn]}
\]

- At the end-point, the indicator is changing colour; this is when \([In^-] = [HIn]\)

- At this point, \(K_a (aka \; K_{HIn}) = [H^+]\) and \(pK_a (aka \; pK_{HIn}) = pH\)
- Note: This is the \(pK_a\) value of the indicator, not that of the acid being titrated!
  \(pK_a(\text{indicator}) = pH \text{ at colour change}\)
- At 1 pH unit below this \(pK_a\) value (acidic) the indicator is 90% in the HIn form.
- At 1 pH unit above this \(pK_a\) value (basic) the indicator is 90% in the \(In^-\) form.
- The approximate range for colour change: 2 pH units.

**Selection of Indicator**

- The indicator must change colour near the equivalence point.
- For a strong acid/strong base titration: the \(pK_a\) of the indicator should be 5 - 9, although in practice the pH changes so rapidly at the end-point that any indicator is suitable.
- For a weak acid/strong base titration: the \(pK_a\) of the indicator must be in the basic region, for example: phenolphthalein, \(pK_a \approx 9\)
- For a strong acid/weak base titration: the \(pK_a\) of the indicator must be in the acidic region, for example: methyl orange, \(pK_a \approx 3.4\)
The Common Ion Effect

- Recall that the common ion effect refers to a system at equilibrium which has present an ion that is present as a result of that equilibrium, but is also present from some other source.
- Consider a solution of Acetic Acid, \( \text{CH}_3\text{COOH} \) \( (K_a = 1.8 \times 10^{-5}) \)

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-
\]

- When we place the acid in water, equilibrium is established very rapidly \( (\approx 10^{-(8\text{-to-10}) \text{ seconds}}) \)......

- What happens (non-quantitatively) to the percent dissociation of the acetic acid \( (\text{CH}_3\text{COOH}) \) if.......

- A strong acid is added to the same solution (so \( \text{H}^+ \) is the added “common ion”)?
- Or, equivalently, the \( \text{CH}_3\text{COOH} \) ionizes into a solution of a strong acid, instead of into water? (For acid-base reactions in water, the order of addition is unimportant.)

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-
\]

2 Sources of \( \text{H}^+ \):

1) from ionization of \( \text{CH}_3\text{COOH} \)
2) from the strong acid (e.g., \( \text{HCl} \))

\[\text{Le Châtelier:} \quad \text{equilibrium shifts away from the H}^+ \]

\[\therefore \text{less CH}_3\text{COOH ionizes} \]
• How do we treat such problems quantitatively?

**EXAMPLE 1:**

A solution is 0.20 M in CH$_3$COOH ($K_a = 1.8 \times 10^{-5}$) and 0.050 M in HCl. What is the % ionization of the CH$_3$COOH? What is the pH of this solution?

- Get $H^+$ from ionization of CH$_3$COOH

CH$_3$COOH $\rightleftharpoons$ H$^+$ + CH$_3$COO$^-$

Ref: 0.20       0.050          0
Eq: 0.20 - $\chi$   $\chi$ + 0.050

\[ K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \]

\[ \frac{1.8 \times 10^{-5}}{0.20} = \frac{(\chi + 0.050)(\chi)}{(0.20 - \chi)} \]

We know that "$\chi$" (amt ionized) is small.
- In presence of a common ion, $\chi$ is even smaller.

\[ 1.8 \times 10^{-5} = \frac{(0.050)(\chi)}{(0.20)} \]

\[ \chi = 7.2 \times 10^{-5} = [CH_3COO^-] \]

% ionization = \[ \frac{\chi}{c} \times 100 = \frac{7.2 \times 10^{-5}}{0.20} \times 100 \]

pH = $[H^+] = 0.05 + \chi = 0.05 + 7.2 \times 10^{-5} = 0.05036$ 7%

pH $\approx 1.30$
A similar situation arises if a weak base dissociates into a solution of a strong base (or, equivalently, a strong base is added to a solution of a weak base).

**EXAMPLE 2:**

In a solution [NaOH] = 0.020 M and [NH₃] = 0.15 M. (K_b = 1.8 x 10⁻⁵)

What is the % ionization of the NH₃? What is the pH of this solution?

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

\[ \text{Byf: } 0.15 \quad \text{Oh: } 0.02 \]

\[ \text{Eq: } 0.15 - x \quad x \quad x + 0.02 \]

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x + 0.02)}{(0.15 - x)} \]

\[ \therefore x = 1.35 \times 10^{-4} = [\text{NH}_4^+] \]

% ionization = \( \frac{x}{C} \times 100 = \frac{1.35 \times 10^{-4}}{0.15} \times 100 = 0.09 \% \)

pH? Basic soln so use pHOH!

\[ [\text{OH}^-] = 0.02 + 1.35 \times 10^{-4} = 2.014 \times 10^{-2} \text{M} \]

pOH = 1.7 \quad \therefore \text{pH} = 12.30
Polyprotic Acids \[MH5;13.4, \text{page 364}\]

- Polyprotic acids are those which have more than one “acidic” hydrogen.
- This means that they dissociate (or ionize) in stages, with $K_a$ values for each step.

**EXAMPLE:** Carbonic acid is $\text{H}_2\text{CO}_3$

Step 1: $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ \hspace{1cm} $K_1 = 4.2 \times 10^{-7}$

Step 2: $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ \hspace{1cm} $K_2 = 4.8 \times 10^{-11}$

Overall: $\text{H}_2\text{CO}_3 \rightleftharpoons 2 \text{H}^+ + \text{CO}_3^{2-}$ \hspace{1cm} $K_{\text{overall}} = K_1 \times K_2$

- These equilibria are typical of polyprotic acids; $K_1 \gg K_2$.
- As a result: $\approx$ all the [H$^+$] is due to the first acid ionization......

- These dissociations also illustrate **simultaneous equilibria** in the acid dissociation of a polyprotic acid; both are happening at the same time.
- So both bicarbonate anion, $\text{HCO}_3^-$, and carbonate anion, $\text{CO}_3^{2-}$, are present in the equilibrium mixture in solution.
EXAMPLE:
Consider the acid dissociation of 0.25 M H₂CO₃.
What are the concentrations of all species in the equilibrium mixture, the % dissociation in each stage, and the pH?
[ K₁ = 4.2 × 10⁻⁷, K₂ = 4.8 × 10⁻¹¹ ]

First acid dissociation:

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{By} & : 0.25 & 0 & 0 \\
\text{Eq} & : 0.25 - x & x & x \\
K_1 & = 4.2 \times 10^{-7} = \frac{x^2}{0.25 - x} \\
\chi & = \sqrt{4.2 \times 10^{-7} \times 0.25} \\
& = 3.24 \times 10^{-4} \\
\text{[H}^+] & = [\text{HCO}_3^-] \\
\% \text{ dissociation} & = \frac{x}{c} \times 100 = \frac{3.24 \times 10^{-4}}{0.25} \times 100 \\
& = 0.13 \% \\
\text{pH} & = -\log (3.24 \times 10^{-4}) \\
& = 3.49
\end{align*}
\]
Second acid dissociation:

Because $K_2 \ll K_1$, the second acid dissociation does not affect either $[H^+]$ or $[\text{HCO}_3^-]$:

$$
\text{HCO}_3^- \leftrightharpoons H^+ + \text{CO}_3^{2-}
$$

Before:

$$
\begin{align*}
&3.24 \times 10^{-4} & 3.24 \times 10^{-4} & 0 \\
&3.24 \times 10^{-4} & 3.24 \times 10^{-4} & y
\end{align*}
$$

Equation:

$$
\begin{align*}
K_a &= \frac{[H^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \\
4.8 \times 10^{-11} &= \frac{(3.24 \times 10^{-4})^2 - y^2}{(3.24 \times 10^{-4} - y)} \\
\therefore y &= 4.8 \times 10^{-11} = [\text{CO}_3^{2-}]
\end{align*}
$$

pH?

$$
\begin{align*}
[H^+] &= 3.24 \times 10^{-4} + 4.8 \times 10^{-11} \\
&= 3.24 \times 10^{-4}
\end{align*}
$$

$$
pH = 3.49
$$

General Result: for a diprotic acid $H_2A$ in water; $[A^{2-}] = K_2$

- Since $K_2$ is very small ($4.8 \times 10^{-11}$), $\text{CO}_3^{2-}$ is quite a strong base
- $K_b = 2.08 \times 10^{-4}$ (from $K_a \times K_b = K_w$).
EXAMPLE: What is the pH of 0.150 M Na₂CO₃ solution?

In water: \[ \text{Na}_2 \text{CO}_3 \rightarrow 2 \text{Na}^+ + \text{CO}_3^{2-} \]

Then the hydrolysis:

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- \]

By! 0.15

\[ K_b = 2.38 \times 10^{-8} \]

\[ K_b (\text{for CO}_3^{2-}) = 2.08 \times 10^{-4}, \]

\[ x = \frac{\sqrt{K_b \times 0.15}}{0.15 - x} \]

\[ = 5.58 \times 10^{-3} = [\text{OH}^-] \]

\[ \text{pOH} = 2.25 \quad \text{pH} = 14 - 2.25 \]

\[ = 11.75 \]

- Further reaction of \( \text{HCO}_3^- \) with \( \text{H}_2\text{O} \) is negligible;
  \[ K_b (\text{HCO}_3^-) = 2.38 \times 10^{-8} \ll K_b (\text{CO}_3^{2-}) = 2.08 \times 10^{-4} \]

Note that \( \text{HCO}_3^- \) may act as either an acid or a base:

In water: \[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}_3^{2-} \] (acid)

\[ \text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \] (base)

OR: If acid or base is added to \( \text{HCO}_3^- \)..................

\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \]

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \]
BUFFERS SOLUTIONS

- So far, we have looked at the behaviour of weak acids and bases in solution, as well as the behaviour of their conjugate species.
- But initially, we have had only the weak acid or base or only the conjugate species present (in water, of course!)
- What happens if we put a weak acid and its conjugate base in the same solution (or, a weak base and its conjugate acid)?
- This type of solution is the one which call a Buffer Solution; probably named as such because these solutions tend to resist changes in pH even when small amounts of strong acid or base are added to them.

- A Buffer Solution contains a weak acid and its conjugate base (or a weak base and its conjugate acid) in roughly equal amounts.
  - within a factor of 10
- A buffer solution can always be treated as a weak acid or base equilibrium, with the conjugate species behaving as a “common ion” (see p. 189 - 191).
- As there are several ways to combine solutions to produce a buffer solution, the trickiest part of dealing with buffer solutions is recognizing that a solution is, in fact, a buffer solution.
- Once recognized, the equilibrium can be set up and the calculation completed.....

- Let’s start with looking at buffers which contain a weak acid and its conjugate base.

- The first examples are straightforward; a weak acid and its conjugate base (in the form of a salt) are mixed together in one solution.
EXAMPLE 1:
A solution contains 0.20 mol acetic acid, $\text{CH}_3\text{COOH}$, and 0.10 mol of sodium acetate, $\text{CH}_3\text{COONa}$, made up to 1.0 L volume. Calculate the pH of the solution. 

$[\text{K}_a \text{ for } \text{CH}_3\text{COOH} = 1.8 \times 10^{-5}]$

$\text{CH}_3\text{COOH} \quad \text{weak acid}$

$\text{CH}_3\text{COONa} \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+$

$\text{conj. base of CH}_3\text{COOH}$

Buffer

$[\text{CH}_3\text{COOH}] = 0.20 \text{ M} \quad [\text{CH}_3\text{COO}^-] = 0.10 \text{ M}$

\[\begin{align*}
\text{Eq.} & \quad \text{CH}_3\text{COOH} \rightleftharpoons H^+ + \text{CH}_3\text{COO}^- \\
\text{Buf.} & \quad 0.20 \quad 0 \quad 0.10 \\
\text{Eq.} & \quad 0.20 - x \quad x \quad 0.10 + x
\end{align*}\]

$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.10 + x)}{(0.20 - x)}$

$x = 3.6 \times 10^{-5}$

$\text{[H}^+] = 3.6 \times 10^{-5}$

$pH = 4.44$
EXAMPLE 2:
What is the pH of the previous solution if it was diluted to a volume of 10.0 L?

\[ \text{After dilution:} \]
\[ [\text{CH}_3\text{COOH}] = \frac{0.2 \text{ mol}}{10.0 \text{ L}} = 0.02 \text{ M} \]
\[ [\text{CH}_3\text{COO}^-] = \frac{0.1 \text{ mol}}{10.0 \text{ L}} = 0.01 \text{ M} \]

\[ \Rightarrow K_a = \frac{[H^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \]

\[ \Rightarrow 1.8 \times 10^{-5} = \frac{(x)(0.01)}{(0.02)} \]

\[ x = 3.6 \times 10^{-5} \]

\[ = [H^+] \quad \therefore \ \text{pH} = 4.44 \]

- What does this result tell us about buffer solutions?
  - Dilution of a buffer solution has no effect on pH
EXAMPLE 3:
What mass, in grams, of NaNO₂ must be added to 700 mL of 0.165 M HNO₂ to produce a solution with a pH of 3.50?

\[ K_a(HNO_2) = 6.0 \times 10^{-4} \]

\[ HNO_2 : \text{weak acid} \]
\[ NaNO_2 \rightarrow Na^+ + NO_2^- \]
\[ \Rightarrow \text{conjugate base of } HNO_2 \]

\[ \therefore \text{Buffer!} \]

\[ pH = 3.50 \quad \therefore [H^+] = 10^{-3.50} = 3.16 \times 10^{-4} \text{ mol L}^{-1} \]

\[ EQ: \quad HNO_2 \rightarrow H^+ + NO_2^- \]

\[ K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} \]

\[ 6.0 \times 10^{-4} = \frac{(3.16 \times 10^{-4})[NO_2^-]}{0.165} \]

\[ [NO_2^-] = 0.313 \text{ mol L}^{-1} \]

\[ \text{mol NO}_2^- = 0.313 \text{ mol L}^{-1} \times 0.700L = 0.219 \text{ mol} = \text{mol NaNO}_2 \]

\[ \text{Mass NaNO}_2 = 0.219 \text{ mol} \times 69 \text{ g mol}^{-1} = 15.1 \text{ g} \]
• But buffer solutions are not only made from weak acids..................
• Let’s look at a buffer solution made from a weak base and its conjugate acid:

EXAMPLE 1:
A solution was prepared by adding 21.5 g of NH₄Cl to 1.50 L of 0.25 M NH₃(aq). Calculate the pH of this solution.  \([K_b \text{ for } NH_3 = 1.8 \times 10^{-5}]\]

\(\text{THINK: } \underline{\text{NH}_3: \text{weak base}}\)

\(\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-\)

\(\text{\underline{Buffer}}\)

\(\text{mol } \text{NH}_4\text{Cl} = \frac{21.5 \text{ g}}{53.5 \text{ g mol}^{-1}} = 0.4019 \text{ mol}\)

\(\text{mol } \text{NH}_4^+ = \text{mol } \text{NH}_3\)

\([\text{NH}_4^+] = \frac{0.4019 \text{ mol}}{1.50 \text{ L}} = 0.2679 \text{ mol L}^{-1}\)

\(\underline{\text{EQ}}\)

\(\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-\)

\(K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}\)

\(1.8 \times 10^{-5} = \frac{(0.2679)[\text{OH}^-]}{(0.25)}\)

\([\text{OH}^-] = 1.68 \times 10^{-5}\)

\(p\text{OH} = 4.77\)

\(p\text{H} = 9.22\)
EXAMPLE 2:

What mass of \( CH_3NH_3Cl \) must be added to 650 mL of a 0.145 M solution of \( CH_3NH_2 \) to produce a solution with pH = 10.50?

\[ [K_b \text{ of } CH_3NH_2 = 6.4 \times 10^{-4}] \]

\[ \underset{\text{wk base.}}{CH_3NH_2} \overset{\text{Buffer}}{\longrightarrow} CH_3NH_3^+ + Cl^- \]

\[ \text{Conj. acid of } CH_3NH_2 \]

\[ \text{EQ: } CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \]

\[ \text{pH} = 10.50 \implies \text{Basic } \implies \text{pOH} = 3.50 \]

\[ \text{pOH} = 10 - 3.50 = 3.16 \times 10^{-4} \text{ M} \]

\[ K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 6.4 \times 10^{-4} \]

Substitute:

\[ 6.4 \times 10^{-4} = \frac{[CH_3NH_3^+](3.16 \times 10^{-4})}{(0.145)} \]

\[ \therefore [CH_3NH_3^+] = 0.294 \text{ mol} L^{-1} \]

\[ \text{mol } CH_3NH_3^+ = 0.294 \text{ mol} L^{-1} \times 0.650 \text{ L} = 0.191 \text{ mol} = \text{mol } CH_3NH_3Cl \]

\[ \text{Mass} = 0.191 \text{ mol} \times 67.5 \text{ g mol}^{-1} \]

\[ = 12.9 \text{ g} \]
Another way of preparing a buffer is to mix an excess of weak acid with a strong base....the reaction produces the conjugate species.

**EXAMPLE 1:**

100 mL of 0.50 M Benzoic Acid, $C_6H_5COOH$, is mixed with 100 mL of 0.20 M $NaOH$. What is the pH of the resulting solution?

$[K_a$ of $C_6H_5COOH = 6.6 \times 10^{-5}]$

\[
\text{Acid and Base} \quad \underline{\text{ALWAYS react first!!!}}
\]

\[
\begin{align*}
\text{mol } C_6H_5COOH &= 0.50M \times 0.100L = 0.050 \text{ mol} \\
\text{mol } NaOH &= 0.20M \times 0.100L = 0.020 \text{ mol} = \text{ mol } OH^- \\
\end{align*}
\]

\[
\begin{align*}
\text{Reax: } C_6H_5COOH + OH^- &\rightarrow H_2O + C_6H_5COO^- \\
\text{Bef: } 0.05 &\quad 0.02 \\
\text{af: } 0.05 - 0.02 &\quad 0 \\
\text{Set up an equilibrium} &\quad \text{Buffer}
\end{align*}
\]

\[
\begin{align*}
[\text{acid}] &= 0.03 \text{ mol} \\
[\text{konj base}] &= 0.02 \text{ mol}
\end{align*}
\]

\[
\begin{align*}
\text{Set up an equilibrium} &\quad \text{Buffer}
\end{align*}
\]

\[
\begin{align*}
\text{Equilibrium} &\quad C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^- \\
\text{Molarity} &\quad K_a = \frac{[H^+] [C_6H_5COO^-]}{[C_6H_5COOH]} \\
6.6 \times 10^{-5} &= [H^+] \left( \frac{0.02 \text{ mol}}{0.03 \text{ mol}} \right) \\
6.6 \times 10^{-5} &= \frac{0.02 \text{ mol}}{0.03 \text{ mol}} [H^+] \\
[H^+] &= 9.90 \times 10^{-5} \\
pH &= 4.00
\end{align*}
\]
EXAMPLE 2:
Calculate the pH of a solution prepared by mixing 150 mL of 0.140 M ammonium chloride, \( \text{NH}_4\text{Cl} \), with 100 mL of 0.112 M KOH. 
\([K_b \text{ for NH}_3 = 1.8 \times 10^{-5}]\)

\[ \text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^- \]
\( \Rightarrow \text{mol} = 0.140 \text{ M} \times 0.150 \text{ L} = 0.021 \text{ mol} \)
\( \text{KOH} \rightarrow \text{K}^+ + \text{OH}^- : \text{st. base} \)
\( \Rightarrow \text{mol} = 0.112 \text{ M} \times 0.100 \text{ L} = 0.0112 \text{ mol} = \text{mol OH}^- \)

\[ \text{Rxn:} \quad \text{NH}_4^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{NH}_3 \]

\begin{align*}
\text{Buffer:} & \quad 0.021 \quad 0.0112 \\
\text{qf:} & \quad 0.021 - 0.0112 \quad 0 \\
\text{calc:} & \quad \frac{0.0098}{\text{conj acid}} \\
\text{Buffer:} & \quad \frac{0.0112}{\text{wk base}}
\end{align*}

\[ \text{EQ:} \quad \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

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

\[ 1.8 \times 10^{-5} = \left( \frac{0.0098 \text{ mol}}{0.250 \text{ L}} \right) [\text{OH}^-] \]

\[ [\text{OH}^-] = 2.057 \times 10^{-5} \text{ M} \quad \therefore \text{pOH} = 4.69 \]

\( \text{pH} = 9.31 \)
What if we could react an excess amount of weak base (which could also be a conjugate base) with a strong acid....the reaction produces the conjugate acid.

**EXAMPLE 1:**

\[ K_b (\text{CH}_3\text{NH}_2) = 6.4 \times 10^{-4} \]  

\( \text{mol HClO}_4 = 0.185 \text{ M} \times 0.150 \text{ L} = 0.01875 \text{ mol} \)  
\( \text{mol H}^+ = \text{mol HClO}_4 \)

\( \text{mol CH}_3\text{NH}_2 = 0.180 \text{ M} \times 0.200 \text{ L} = 0.036 \text{ mol} \)

\[ \text{Reaction:} \quad \text{H}^+ + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ \]

\[ \text{Eq:} \quad 0.01875 \quad 0.036 \]
\[ \text{Eq:} \quad 0 \quad 0.036 - 0.01875 \]
\[ \text{Eq:} \quad = 0.01875 \]

\[ \text{Eq:} \quad \text{Buffer:} \quad \text{CH}_3\text{NH}_3^+ + \text{OH}^- \]

\[ K_b = 6.4 \times 10^{-4} = \frac{(0.01875)[OH^-]}{(0.01875)} \]

\[ [OH^-] = 5.89 \times 10^{-4} \Rightarrow pOH = 3.23 \Rightarrow pH = 10.77 \]

**EXAMPLE 2:** What is the reaction that would occur between excess potassium nitrite, KNO\(_2\), and HNO\(_3\)?

Need \( K_a \) for HNO\(_2\)  

\( \text{KNO}_2 \rightarrow \text{K}^+ + \text{NO}_2^- \)  

\( \text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^- \)

\[ \text{Reaction:} \quad \text{H}^+ + \text{NO}_2^- \rightarrow \text{HNO}_2 \]
• On p. 196 we mentioned that buffer solutions tend to resist large changes in pH, even when small amounts of strong acid or base are added to them.
• How do they do this, and does one calculate any change in pH of a buffer solution?

**EXAMPLE 1:**

0.20 mol of formic acid, HCOOH, and 0.15 mol of sodium formate, HCOONa, are made up to 1.0 L volume, to give a solution having pH = 3.60. What happens to the pH if we add 0.03 mol of HCl to this solution? \( [K_a \text{ of HCOOH} = 1.9 \times 10^{-4}] \)

\[
\begin{align*}
\text{HCOOH} & \quad \text{weak acid} \quad \text{mol} = 0.20 \\
\text{HCOONa} \rightarrow \text{HCOO}^- + \text{Na}^+ \quad \text{mol} = 0.15 \\
\Rightarrow \text{buffer}
\end{align*}
\]

\[
\text{pH} = 3.60 \implies [H^+] = 10^{-3.60} = 2.51 \times 10^{-4} \text{ M}
\]

Add 0.03 mol of HCl = 0.03 mol H^+

\[
\begin{align*}
\text{Run} & \quad \text{HCOOH} \leftrightharpoons H^+ + \text{HCOO}^- \\
0.20 & \quad 0.03 \\
0.20 + 0.03 & \quad 0 \\
0.23 & \quad 0.15 - 0.03 \\
& \quad 0.12
\end{align*}
\]

\[
\begin{align*}
\text{Eq} & \quad \text{HCOOH} \leftrightharpoons H^+ + \text{HCOO}^- \\
K_a & = \frac{[H^+] [\text{HCOO}^-]}{[\text{HCOOH}]} \implies 1.9 \times 10^{-4} = \frac{[H^+]}{(0.23 \text{ mol})} (0.12 \text{ mol})
\end{align*}
\]

\[
[H^+] = 3.64 \times 10^{-4} \quad \therefore \text{pH} = 3.43
\]

\[
\Delta \text{pH} = 3.60 - 3.43 = 0.17
\]
Obviously, we could also add strong base to this buffer solution.

\[ \text{pH} = 3.80 \]

**EXAMPLE 2:**
0.20 mol of formic acid, HCOOH, and 0.15 mol of sodium formate, HCOONa are made up to 1.0 L volume, to give a solution having pH = 3.60. Then 1.60 g of NaOH are added to the solution. What is the change in the pH? \( [K_a \text{ of HCOOH} = 1.9 \times 10^{-4}] \)

\[
\begin{align*}
\text{mol HCOOH} &= 0.20 \\
\text{mol HCOO}^- &= 0.15 \\
\text{mol NaOH} &= \frac{1.60 \text{ g}}{40 \text{ g mol}^{-1}} = 0.04 \text{ mol} = \text{mol OH}^- \\
\end{align*}
\]

**Reaction:** what reacts with OH\(^-\)?

\[
\begin{align*}
\text{HCOOH} + \text{OH}^- &\rightarrow \text{HCOO}^- + \text{H}_2\text{O} \\
0.20 &\quad 0.04 \\
0.20 - 0.04 &\quad 0 \\
= 0.16 &\quad 0.15 + 0.04 \\
\text{weak acid} &\quad \text{Buffer} \\
\end{align*}
\]

**EQ**

\[
\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^- \\
K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \\
1.9 \times 10^{-4} = \frac{[\text{H}^+](0.19 \text{ mol})}{(0.16 \text{ mol})(1.0)} \\
\therefore [\text{H}^+] = 1.6 \times 10^{-4} \Rightarrow \text{pH} = 3.80
\]

\text{pH is 0.20 units higher}
EXAMPLE 3:

What change in pH would occur if we added the same amounts of HCl (as in Ex. 1) and NaOH (as in Ex. 2) to 1.0 L of just water (instead of buffer)?

\[
\text{mol HCl} = 0.03 \text{ mol} = \text{mol } H^+ \\
[H^+] = \frac{0.03 \text{ mol}}{1.0 \text{ L}} = 0.03 \text{ M} \\
\text{pH} = 1.52
\]

\[
\text{mol NaOH} = 0.04 \text{ mol} = \text{mol OH}^- \\
[OH^-] = \frac{0.04 \text{ mol}}{1.0 \text{ L}} = 0.04 \text{ M} \\
\text{pOH} = 1.40 \quad \Rightarrow \quad \text{pH} = 12.60
\]
EXAMPLE 2:
A solution contains 0.60 mol of NH₄Cl and 0.30 mol of NH₃(aq) in 1.5 L. The pH of the solution is 8.95. What will be the change in pH if we add 0.07 mol of HCl to this solution? 

\[ K_b(\text{NH}_3) = 1.8 \times 10^{-5} \]

\[ \text{NH}_3 \text{ (weak base): mol} = 0.30 \text{ mol} \quad \text{Buffer} \]

\[ \text{NH}_4^+ \text{Cl} \rightarrow \text{NH}_4^+ \text{ + Cl}^- \]

\[ \text{Conjugate acid of NH}_3 \text{ mol} = 0.60 \text{ mol} \]

\[ \text{Equation: } \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \]

\[ \text{Reactants: } 0.30 \quad 0.07 \quad 0.60 \]

\[ \text{Products: } 0.23 \quad 0 \quad 0.67 \]

\[ \text{Weak base buffer} \quad \text{Conjugate acid} \]

\[ \text{Equation: } \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \]

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

\[ 1.8 \times 10^{-5} = \frac{(0.67 \text{ mol})[\text{OH}^-]}{(0.33 \text{ mol})} \]

\[ [\text{OH}^-] = 6.1 \times 10^{-6} \]

\[ \text{pOH} = 5.21 \quad \Rightarrow \quad \text{pH} = 8.79 \]

pH dropped by 0.16 pH units.
1) **Strong Acid - Strong Base:**
There is no buffering action and the pH changes **abruptly** at the equivalence point.

\[
\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl} \\
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

![Diagram showing pH changes for strong acid-strong base titration](image)

- **Equivalence Point**
  - mol H\(^+\) = mol OH\(^-\)
- **Excess H\(^+\)**
- **Excess OH\(^-\)**

**Vol base added**
2) **Weak acid - Strong Base:**
Adding strong base to a weak acid, the solution is buffered before the equivalence point, where we have the acid + conjugate base present.
The pH changes slowly and the solution is basic at the equivalence point.
The “vertical step around equivalence is < in (1), so choice of indicator more important.
3) **Strong Acid - Weak Base:**

Adding weak base to a strong acid, the solution is not buffered until after the equivalence point.

Before the equivalence point, the pH of the solution is controlled by the strong acid.

After the equivalence point, there exists the mixture of weak base and its conjugate acid.

The pH changes very slowly before the equivalence point; at which the solution is acidic.

The "vertical step around equivalence is \(< in (1), so choice of indicator more important."

\[ \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \]