Chemistry 201

Lecture 14

Acid and base mixtures
Introduction to buffers

NC State University
Goals

• Convert between $K_a$, $pK_a$, $K_b$ and $pK_b$
• Calculate the pH of solutions of weak acids and weak bases
• Understand titrations as quantitative chemical analysis
know $[\text{H}_3\text{O}^{1+}]$ calc pH

know $[\text{OH}^{1-}]$ calc pOH

Strong Acid

Weak Acid

Strong Base

Weak Base
know $[\text{H}_3\text{O}^{1+}]$ calc pH
text
know $[\text{OH}^{1-}]$ calc pOH
text

Strong Acid

Strong Base

Weak Acid

Weak Base

rxn table use $K_a$ get $[\text{H}_3\text{O}^{1+}]$ calc pH
Relationship of \( pK_a \) and \( pK_b \)

\[
HA + H_2O \leftrightarrow A^- + H_3O^+ \\
K_a = \frac{[A^-][H^+]}{[HA]}
\]

\[
A^- + H_2O \leftrightarrow HA + OH^- \\
K_b = \frac{[HA][OH^-]}{[A^-]}
\]

\[
H_2O + H_2O \leftrightarrow OH^- + H_3O^+ \\
K_w = [H^+][OH^-]
\]

\[
\left(\frac{[A^-][H^+]}{[HA]}\right)\left(\frac{[HA][OH^-]}{[A^-]}\right) = [H^+][OH^-]
\]

\[
K_aK_b = K_w
\]

\[
pK_a + pK_b = pK_w
\]
pH of Weak Bases

What is the pH of a 0.10 M solution of NaF? \((pK_a = 3.14\) for HF)
pH of Weak Bases

What is the pH of a 0.10 M solution of NaF? (pK\textsubscript{a} = 3.14 for HF)

Solution: Write down the conjugate base reaction

\[ F^- + H\textsubscript{2}O \leftrightarrow HF + OH^- \]

Step 1: Solve for \( K\textsubscript{b} \)

\[
pKb = pKw - pK\textsubscript{a}
\]

\[
pKb = 14 - 3.14 = 10.86
\]

\[
K_b = 10^{-pKb} = 10^{-10.86} = 1.38 \times 10^{-11}
\]
pH of Weak Bases

NaF problem (contd)  (pK\textsubscript{a} = 3.14 for HF)

Step 2: Make an ICE reaction table

<table>
<thead>
<tr>
<th>Molecule</th>
<th>F\textsuperscript{-}</th>
<th>HF</th>
<th>OH\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Difference</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.1-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Step 3: Solve for x

\[ K_b 0.1 - K_b x - x^2 = 0 \]

\[ x = \frac{K_b \pm \sqrt{K_b^2 + 4(0.1)K_b}}{-2} \]

\[ x = \frac{1.38 \times 10^{-11} \pm \sqrt{(1.38 \times 10^{-11})^2 + 0.4(1.38 \times 10^{-11})}}{-2} \]

\[ x = 1.17 \times 10^{-6} \]
pH of Weak Bases

NaF problem (contd) \( (pK_a = 3.14 \text{ for HF}) \)

Step 4: Solve for \( pOH \)

\[
pOH = -\log_{10}(1.17 \times 10^{-6}) = 5.93
\]

Step 5: Convert to \( pH \)

\[
pH + pOH = pK_w
\]

\[
pH = pK_w - pOH
\]

\[
pH = 14 - 5.93 = 8.07
\]
Strong Acid

Weak Acid

Strong Base

Weak Base

know \([H_3O^{1+}]\)
calc pH

know \([OH^{1-}]\)
calc pOH

rxn table
use \(K_a\)
get \([H_3O^{1+}]\)
calc pH
Strong Acid

Know [H$_3$O$^{1+}$]
Calc pH

Strong Base

Know [OH$^{1-}$]
Calc pOH

Weak Acid

Rxn table
Use $K_a$
Get [H$_3$O$^{1+}$]
Calc pH

Weak Base

Rxn table
Use $K_b$
Get [OH$^{1-}$]
Calc pOH and pH
Titration: quantitative analysis

**Titration** is a laboratory method of quantitative analysis used to determine unknown concentration of an analyte. We can also call it volumetric analysis. First, we prepare a standard solution of the titrant. Then we measure how much titrant is required to produce an optical change. pH titrations are only one kind of titration. Typically, we will use a pH indicator and add a known volume of acid to base (or base to an acid). The end point is reached when the indicator changes color. One of the most common indicators in pH titrations is phenolphthalein.
pH indicators: phenolphthalein

Phenolphthalein changes color at pH 8.2.

Colorless → Pink
Titration

The procedure is to use a buret to accurately dispense a known volume of the titrant. The endpoint is reached when the unknown solution changes color. We add a very small amount of indicator to the unknown in order to see the color change.
Titration

If a base is neutralized by acid then we can assume that dilution factor of the acid times its known concentration gives us the concentration of the base.

\[ C_a = \frac{V_t}{V_a} C_t \]

If the stoichiometry of the analyte and titrant is not 1:1 then we need to multiply by the appropriate factor.
Titration when the stoichiometry is not 1:1

If we want to determine the amount of oxalic acid dissolved in water, we can add a known amount of NaOH until the equivalence point is reached.

$$2 \text{ NaOH} + C_2\text{O}_4\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{C}_2\text{O}_4$$

In this case, we require two moles of NaOH for each mole of oxalic acid. The concentration of the analyte is:

$$C_a = \frac{V_t v_a}{V_a v_t} C_t$$

Where $v_a$ and $v_t$ are the stoichiometric coefficients.
Strong Acid

Strong Base

Weak Acid

Weak Base

pH dictated by strong acid

pH dictated by strong base
The pH of a solution is dictated by the concentration of strong acid or strong base. At the equivalence point, the pH changes:

- pH at equivalence point $C_1V_1$
- pH at equivalence point $C_2V_2$
Part 2: Goals

- Learn how to make a buffer
- Understand the strategy for choosing buffer components
- Be able to read a titration curve and understand it
two bases
equiv. pt.
buffer
weak acid

Figure 7.3

The buffer region is shown in the orange
Mixture of acid and conjugate base
Making a buffer

What is the pH of a solution made by adding 0.50 g of NaC₂H₃O₂ to 50.0 mL of 0.15 M HC₂H₃O₂? (Assume V change is negligible.) [HC₂H₃O₂ is acetic acid]

Step 1. Determine concentrations

\[ n = \frac{0.50\,g}{82\,g/mol} = 0.00609\,mol\,NaC₂H₃O₂ \]

\[ M(\text{NaC}_2\text{H}_3\text{O}_2) = \frac{0.00609\,mol}{0.05\,L} = 0.121\,M \]
Step 2. Write down the equilibrium expression and make a reaction table.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>CH₃COOH</th>
<th>CH₃COO⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.15</td>
<td>0.121</td>
<td>0.0</td>
</tr>
<tr>
<td>Difference</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Final</td>
<td>0.15-x</td>
<td>0.121+x</td>
<td>x</td>
</tr>
</tbody>
</table>

Step 3. Solve for \(x\)

\[ K_a = \frac{x(0.12 + x)}{(0.15 - x)} \]

\[ K_a(0.15 - x) = 0.12x + x^2 \]

\[ 0.15K_a - (K_a + 0.12)x - x^2 = 0 \]
Step 3. (contd) Solve for $x$
Now we need the $K_a$. Look up the p$K_a$. $pK_a = 4.74$

\[
x = \frac{(K_a + 0.12) \pm \sqrt{(K_a + 0.12)^2 + 4(0.15)K_a}}{-2}
\]

\[
x = \frac{(1.8 \times 10^{-5} + 0.12) \pm \sqrt{(1.8 \times 10^{-5} + 0.12)^2 + 4(0.15)1.8 \times 10^{-5}}}{-2}
\]

Step 4. Calculate $pH$

\[
pH = -\log_{10}(2.24 \times 10^{-4})
\]

$pH = 4.65$
We just did this the hard way!

Given that we have

\[ [\text{CH}_3\text{COO}^-] = 0.121 \text{ M} \] and

\[ [\text{CH}_3\text{COOH}] = 0.15 \text{ M} \]

What is the pH of the buffer?

\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right)
\]

\[
\text{pH} = 4.74 + \log_{10} \left( \frac{0.121}{0.15} \right) = 4.65
\]

We obtain the same answer using the H-H equation.
Add 0.01 M HCl to this buffer

What is the pH of this solution if we add 0.01 M of HCl to it?
What is the pH of this solution if we add 0.01 M of HCl to it?
Now we have
$[\text{CH}_3\text{COO}^-] = 0.111 \text{ M}$ and
$[\text{CH}_3\text{COOH}] = 0.16 \text{ M}$
Use H-H equation

$$
\text{pH} = 4.74 + \log_{10} \left( \frac{0.111}{0.16} \right) = 4.58
$$
What is the pH of this solution if we add 0.01 M of HCl to it?

Now we have

$[\text{CH}_3\text{COO}^-] = 0.111 \text{ M}$ and
$[\text{CH}_3\text{COOH}] = 0.16 \text{ M}$

Use H-H equation

$$\text{pH} = 4.74 + \log_{10}\left(\frac{0.111}{0.16}\right) = 4.58$$

If no buffer were present we would have had

$$\text{pH} = -\log_{10}([\text{HCl}]_0) = -\log_{10}(0.02) = 2$$
Relationship between pH and pKa

Henderson-Hasselbach equation

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

\[ -\log_{10} K_a = -\log_{10} \left( \frac{[A^-]}{[HA]} \right) - \log_{10} [H^+] \]

\[ \text{pH} = \text{pK}_a + \log_{10} \left( \frac{[A^-]}{[HA]} \right) \]

Useful for estimating protonation states.
For example, when \([HA]= [A^-]\) then \(\text{pK}_a = \text{pH}\).
If \([A^-]/[HA] = 10\), then \(\text{pK}_a = \text{pH} + 1\).
If \([A^-]/[HA] = 0.1\), then \(\text{pK}_a = \text{pH} - 1\).
if conjugates use H-H

calculate pH

pH dictated by strong acid

pH dictated by strong base

Strong Acid

Weak Acid

Strong Base

Weak Base
Buffer Strategy

The Hendersen-Hasselbach equation gives us a strategy for making buffers. You want lot of the acid and its conjugate base. If those two are equal in concentration (stable!) then we have

\[ \text{pH} = \text{pK}_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \]

where \([HA] \sim [A^-]\) so

\[ pK_a = pH \]

This is a good criterion of an buffer.
Buffer Strategy

What conjugate pair would you use to produce
- a pH 7 buffer?
- a pH 9 buffer?
Phosphate buffer

How many grams of Na$_2$HPO$_4$ ($M_m = 142$ g/mol) would you add to 100 mL of 0.5 M NaH$_2$PO$_4$ to make a pH = 7.40 “phosphate buffer”?

Solution: use Henderson-Hasselbach

$$K_2 = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]}$$

$$K_2 = 6.2 \times 10^{-8}$$

$$pH = pK_a + \log_{10}\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right)$$

which can be written as

$$[HPO_4^{2-}] = [H_2PO_4^-]10^{pH-pK_a}$$
Phosphate buffer

How many grams of Na$_2$HPO$_4$ ($M_m = 142$ g/mol) would you add to 100 mL?

Calculate the concentration needed

\[ [H_2PO_4^-] = [0.5]10^{7.4-7.2} = 0.79 \]

and then the mass. The volume is 100 mL so the number of moles is:

\[ n = (0.79 \text{ M})(0.1 \text{ L}) = 0.079 \text{ moles} \]

and the mass is

\[ m = nM_m = (0.079 \text{ moles})(142 \frac{g}{\text{mol}}) \]

m = 11.2 grams.
from H-H:  
\[ \text{pH} = pK_a \]

equal amts  
HA & A\(^{1-}\)

halfway to  
equiv. pt.
Practical phosphate buffer

How many grams of $\text{Na}_2\text{HPO}_4$ ($M_m = 142 \text{ g/mol}$) and $\text{NaH}_2\text{PO}_4$ ($M_m = 120 \text{ g/mol}$) would you need to weigh out to make 1L of a 100 mM phosphate buffer at $\text{pH} = 7.00$?

Solution: use Henderson-Hasselbach

$$pH = pK_a + \log_{10}\left(\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}\right)$$

to determine the ratio of concentrations in the final buffer.

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{7.0-7.2} = 10^{-0.2} = 0.630$$
Practical phosphate buffer

How many grams of Na$_2$HPO$_4$ ($M_m = 142$ g/mol) and NaH$_2$PO$_4$ ($M_m = 120$ g/mol) would you need to weigh out to make 1L of a 100 mM phosphate buffer at pH = 7.00?

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+
\]

\[
0.1 - x \quad \rightarrow \quad x \quad \text{x}
\]

\[
\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.630 \quad \frac{0.1 - x}{x} = 0.630 \quad 0.1 = 1.630x
\]

\[
x = \frac{0.1}{1.630} = 0.0613
\]
Practical phosphate buffer

How many grams of Na$_2$HPO$_4$ ($M_m = 142$ g/mol) and NaH$_2$PO$_4$ ($M_m = 120$ g/mol) would you need to weigh out to make a 100 mM phosphate buffer at pH = 7.00?

\[
\begin{align*}
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} & \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+ \\
0.1 - x & \rightarrow x \\
\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} & = 0.630 \\
\frac{0.1 - x}{x} & = 0.630 \\
0.1 & = 1.630x \\
x & = \frac{0.1}{1.630} = 0.0613
\end{align*}
\]
Practical phosphate buffer

How many grams of Na$_2$HPO$_4$ ($M_m = 142$ g/mol) and NaH$_2$PO$_4$ ($M_m = 120$ g/mol) would you need to weigh out to make a 100 mM phosphate buffer at pH = 7.00?

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+
\]

NaH$_2$PO$_4$  (0.0613 mole) \( \left( \frac{120 \text{ g}}{\text{mole}} \right) = 7.35 \text{ g} \)

Na$_2$HPO$_4$  (0.0387 mole) \( \left( \frac{142 \text{ g}}{\text{mole}} \right) = 5.49 \text{ g} \)
weak base buffer
equiv. pt.
two acids

Figure 7.5
Ch. 7 : Acid/Base Mixtures

• **Cases with no reaction**
  – acid + acid
  – base + base
  – both halves of conjugate pair

• **Cases with reactions**
  – acid + base
Acid/Base Mixtures: Common Ions and Buffers

- What happens to pH when you mix 2 acids (or 2 bases)?

- What happens to pH when you mix a conjugate pair?

Text: Sections 7.0 - 7.2
pH dictated by strong acid

Strong Acid
Weak Acid

pH dictated by strong base

Strong Base
Weak Base
Common ion effect

What are the conc. of all species and the pH when 10.0 mL of 0.150 M HCl are added to 40.0 mL of 0.250 M HC$_2$H$_3$O$_2$?

these are not “initial concs.” because of the dilution effect
Step 1. Determine concentrations after mixing

For HCl, the dilution factor is 1/5
\[ [\text{HCl}] = 0.150 \text{ M}(1/5) = 0.030 \text{ M} \]

For HC\(_2\)H\(_3\)O\(_2\) the dilution factor is 4/5
\[ [\text{HC}\(_2\)H\(_3\)O\(_2\)] = 0.250 \text{ M}(4/5) = 0.200 \text{ M} \]

Step 2. Write the equilibrium constant and Make a reaction table.

\[
K_a = \frac{[\text{CH}_3\text{COO}^-][H^+]}{[\text{CH}_3\text{COOH}]} 
\]
Step 2. (contd) Make a reaction table.

<table>
<thead>
<tr>
<th>Species</th>
<th>CH₃COOH</th>
<th>CH₃COO⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.20</td>
<td>0</td>
<td>0.030</td>
</tr>
<tr>
<td>Difference</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Final</td>
<td>0.2-x</td>
<td>x</td>
<td>0.03+x</td>
</tr>
</tbody>
</table>

Step 3. Solve for x.

\[
K_a = \frac{x(0.03 + x)}{(0.2 - x)}
\]

\[
K_a(0.2 - x) = 0.03x + x^2
\]

\[
0.2K_a - (K_a + 0.03)x - x^2 = 0
\]

\[
x = \frac{(K_a + 0.03) \pm \sqrt{(K_a + 0.03)^2 + 4(0.2)K_a}}{-2}
\]
Step 3. (contd) Solve for $x$
Using the value of 4.74 for the pKa of acetic acid we have.

\[ x = \frac{(1.8 \times 10^{-5} + 0.03) \pm \sqrt{(1.8 \times 10^{-5} + 0.03)^2 + 4(0.2)K_a}}{-2} \]

Which gives $x = 1.12 \times 10^{-4}$ M.
The total $[H^+]$ is $0.03 + 1.12 \times 10^{-4}$ M
which gives $[H^+] = 0.0301$ M

Step 4. Convert to pH.

\[ pH = -\log_{10}(0.03011) \]

$pH = 1.52$
Note that $x$ is negligible in this problem. This leads us to suggest an alternative method.

\[
x \approx \frac{0.2}{0.03} K_a
\]

\[
x \approx \frac{0.2}{0.03} (1.8 \times 10^{-5})
\]

\[
x \approx 1.12 \times 10^{-4}
\]
Note that $x$ is negligible in this problem. This leads us to suggest an alternative method.

$$x \approx \frac{0.2}{0.03} K_a$$

$$x \approx \frac{0.2}{0.03} (1.8 \times 10^{-5})$$

$$x \approx 1.12 \times 10^{-4}$$

Then test whether $x << \text{[initial concentrations]}$
Note that $x$ is negligible in this problem. This leads us to suggest an alternative method.

\[ x \approx \frac{0.2}{0.03} K_a \]

\[ x \approx \frac{0.2}{0.03} (1.8 \times 10^{-5}) \]

\[ x \approx 1.12 \times 10^{-4} \]

Then test whether $x \ll [\text{initial concentrations}]$

\[ \frac{x}{[CH_3COOH]} = \frac{1.12 \times 10^{-4}}{0.2} 100\% = 0.06\% \]

\[ \frac{x}{[H^+]} = \frac{1.12 \times 10^{-4}}{0.03} 100\% = 0.4\% \]

Yes!