Chapter 15 Aqueous Equilibrium

Buffers and other phenomena
Review

• Recall when you hydrolyze a weak base the reaction looks like this:

  \[
  \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH} + \text{OH}^- \\
  \text{base} \quad \text{acid} \quad \text{conj} \quad \text{conj} \quad \text{acid} \quad \text{base}
  \]
Buffered solutions

• Resist changes in pH when an acid or a base is added.

• Are made from
  – A weak acid and its salt
  – A weak base and its salt
Acid-Salt buffers

• Acid must be a weak acid. This means it has a reservoir of molecules from which a proton can be separated if the need arises.

• The salt is made with the common anion of the acid (the acid’s conjugate base) and the cation of a strong base. Example $\text{NaC}_2\text{H}_3\text{O}_2$ can be thought of as resulting from $\text{NaOH} + \text{HC}_2\text{H}_3\text{O}_2$. 
Some examples of Acid/Salt pairs

<table>
<thead>
<tr>
<th>Weak Acid</th>
<th>Formula of the acid</th>
<th>Example of a salt of the weak acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrofluoric</td>
<td>HF</td>
<td>KF - Potassium fluoride</td>
</tr>
<tr>
<td>Formic</td>
<td>HCOOH</td>
<td>KHCOO - Potassium formate</td>
</tr>
<tr>
<td>Benzoic</td>
<td>C₆H₅COOH</td>
<td>NaC₆H₅COO - Sodium benzoate</td>
</tr>
<tr>
<td>Acetic</td>
<td>CH₃COOH</td>
<td>NaH₃COO - Sodium acetate</td>
</tr>
<tr>
<td>Carbonic</td>
<td>H₂CO₃</td>
<td>NaHCO₃ - Sodium bicarbonate</td>
</tr>
<tr>
<td>Propanoic</td>
<td>HC₃H₅O₂</td>
<td>NaC₃H₅O₂ - Sodium propanoate</td>
</tr>
<tr>
<td>Hydrocyanic</td>
<td>HCN</td>
<td>KCN - potassium cyanide</td>
</tr>
</tbody>
</table>
Base/Salt Buffers

- The salt in a base-salt buffer will include the cation of the base, and an anion that comes from a strong acid. Common anions would be chloride (HCl) and nitrate (HNO₃).
## Base/salt pairs

<table>
<thead>
<tr>
<th>Base</th>
<th>Formula of the base</th>
<th>Example of a salt of the weak acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
<td>$\text{NH}_4\text{Cl}$ - ammonium chloride</td>
</tr>
<tr>
<td>Methylamine</td>
<td>$\text{CH}_3\text{NH}_2$</td>
<td>$\text{CH}_3\text{NH}_2\text{Cl}$ - methylammonium chloride</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>$\text{C}_2\text{H}_5\text{NH}_2$</td>
<td>$\text{C}_2\text{H}_5\text{NH}_3\text{NO}_3$ - ethylammonium nitrate</td>
</tr>
<tr>
<td>Aniline</td>
<td>$\text{C}_6\text{H}_5\text{NH}_2$</td>
<td>$\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ - aniline hydrochloride</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$\text{C}_5\text{H}_5\text{N}$</td>
<td>$\text{C}_5\text{H}_5\text{NHCl}$ - pyridine hydrochloride</td>
</tr>
</tbody>
</table>
Why do buffers work

• Consider an aqueous solution of HF:
  \[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \]  according to LeChatelier’s principle, what would happen to the pH if we add NaF?

• \[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \]

• \[ \text{Na} \rightleftharpoons \text{Na}^+ + \text{F}^- \]

• This would result in

• \[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- + \text{Na}^+ \]  the common ion reverses the dissociation of HF and so more is molecular. pH goes up.
Base example of common ion

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

- Adding the common ion crowds the NH$_4^+$, this leads to less OH$^-$ being formed in the first reaction. pH goes down.
Acid/Salt buffer example

• Calculate the pH of a buffer system containing 1.0 M HF (Ka = 7.2 \times 10^{-4}) and 1.0 M NaF.

• HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)

• Ka = \frac{[H^+][F^-]}{[HF]} = 7.2 \times 10^{-4} [HF]
Example cont’d

<table>
<thead>
<tr>
<th></th>
<th>HF−</th>
<th>H+</th>
<th>F−</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>1.0 −x</td>
<td>x</td>
<td>1.0 +x</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Example continued

- \[ x(1.0 + x) = 7.2 \times 10^{-4} \]
- \[ 1.0 - x \]
- simplifies (usually)
- \[ x(1.0) = 7.2 \times 10^{-4} \]
- \[ 1.0 \]
- \[ x = 7.2 \times 10^{-4} \]
- \[ pH = 3.14 \]
### Example cont’d

<table>
<thead>
<tr>
<th></th>
<th>HF-</th>
<th>H+</th>
<th>F-</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>1.0 (-x)</td>
<td>(x)</td>
<td>1.0 (+x)</td>
</tr>
<tr>
<td>E</td>
<td>1.0</td>
<td>7.2 (\times 10^{-4})</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Couple of useful equations!!!

- When dealing with buffers, keep in mind:
  - \([H^+] = Ka\frac{[HA]}{[A^-]}\)

- In buffer problems HA and A- are known as is Ka:
  - \(pH = pKa + \log\frac{[A^-]}{[HA]} = pKa + \log\frac{[base]}{[acid]}\)
2nd Acid/Salt buffer

• Calculate the pH of a solution which contains 0.50 M acetic acid (HC$_2$H$_3$O$_2$  Ka = 1.8 x 10$^{-5}$) and 0.50 M sodium acetate.

• What are the possible ions in solution HC$_2$H$_3$O$_2$, Na$^+$, C$_2$H$_3$O$_2^-$, and H$_2$O

• What reaction will control equilibrium

• HC$_2$H$_3$O$_2$ $\rightleftharpoons$ H$^+$ + C$_2$H$_3$O$_2^-$
Example 2 cont’d

• Write the Ka expression
• \[ Ka = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \]
• Set up and ice table and write an expression for the changes
## ICE Table

<table>
<thead>
<tr>
<th></th>
<th>HAc⁻</th>
<th>H⁺</th>
<th>Ac⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.50</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>C</td>
<td>0.50</td>
<td>-x</td>
<td>x</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td>0.50 + x</td>
</tr>
</tbody>
</table>
Substitute and Solve

• \(1.8 \times 10^{-5} = \frac{(x)(0.50 + x)}{(0.50 - x)}\)

• Since \(K_a\) is small then \(x\) should be small we can simplify this to:

• \(1.8 \times 10^{-5} = (x)(0.50)\)

• \(1.8 \times 10^{-5} = x\) \((x\) is less than \(5\%\)\)

• \(pH = 4.74\)
pH change in a buffer problem

• Now take this buffer system and add 0.010 mol solid NaOH.

• What are the species present in water:
  • $\text{HC}_2\text{H}_3\text{O}_2$, $\text{Na}^+$, $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{OH}^-$, and $\text{H}_2\text{O}$

• $\text{OH}^-$ will cause $\text{HC}_2\text{H}_3\text{O}_2$ to lose $\text{H}^+$ to neutralize $\text{OH}^-$
pH change

• 1 do the stoichiometry of the problem, then worry about eqm.
• Reaction:
• $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$
ICE Table it

<table>
<thead>
<tr>
<th></th>
<th>HAc-</th>
<th>OH-</th>
<th>Ac-</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.0 L x .50 M</td>
<td>0.010 mol</td>
<td>1.0 L x .50 M = 0.50 mol</td>
</tr>
<tr>
<td></td>
<td>= 0.50 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.50 –0.010</td>
<td>- 0.010 mol</td>
<td>0.50 + 0.01 mol</td>
</tr>
<tr>
<td></td>
<td>0.49 mol</td>
<td>0.0 mol</td>
<td>0.51 mol</td>
</tr>
</tbody>
</table>
pH change cont’d

• Now substitute this into a Ka expression

• \[ 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \]

• \[ 1.8 \times 10^{-5} = (x)(0.51 + x) \frac{1}{(0.49-x)} \]

• Since Ka is small simplify to:

• \[ (x)(0.51) = 1.8 \times 10^{-5} \]

• \[ (0.49) \]
pH change cont’d

- $X = [H+] = 1.7 \times 10^{-8}$
- $\log 1.7 \times 10^{-8} = 4.76$
- the orginal solution had a pH of 4.74!
- pH hardly budged!!!!
- If we had added this much NaOH to pure water the pH would have ended at 12.00!!!
- Buffers really do work.
pH of a buffer and pH change

• A buffered solution contains 0.25 of NH$_3$ (K$_b$ = 1.8 x 10$^{-5}$) and 0.40 M NH$_4$Cl What is the pH of this solution
• Write the major species in solution

• Write a Kb expression.
pH of a buffer and pH change

<table>
<thead>
<tr>
<th>NH₃</th>
<th>NH₄⁺</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>C</td>
<td>0.25−x</td>
<td>0.40+x</td>
</tr>
</tbody>
</table>

Substitute and solve the Kb
Substituting and solvation ;)

- \( K_b = (0.40 + x) x \)
- \( 0.25 - x \)
- Since \( K_b \) is small
- \( K_b = (0.40) x = 1.8 \times 10^{-5} \)
- \( 0.25 \)
- \( x = 1.1 \times 10^{-5} \)
# pH of a buffer and pH change

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$</th>
<th>NH$_4^+$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.25</td>
<td>0.40</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0.25–x</td>
<td>0.40 + x</td>
<td>+ x</td>
</tr>
<tr>
<td>E</td>
<td>0.25</td>
<td>0.40</td>
<td>1.1x10$^{-5}$</td>
</tr>
</tbody>
</table>
So what is the pH?

- \((-\log (1.1 \times 10^{-5})) = 4.95 = \text{pOH}\)
- \(\text{pH} = 9.05\)

- pH without the common ion would’ve been 11.3 !!!
Ex. 2 pH of buffer solution

- What is the pH of a solution of 0.75M lactic acid (HC$_3$H$_5$O$_3$) and sodium lactate 0.25 M. Ka = 1.4 x 10$^{-4}$
- HLac, Lac$^-$, Na$^+$ and H$_2$O major species
- HC$_3$H$_5$O$_3$ $\rightleftharpoons$ H$^+$ + C$_3$H$_5$O$_3^-$
- Ka = $\frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = 1.4 \times 10^{-4}$
**pH of a buffer**

<table>
<thead>
<tr>
<th></th>
<th>HLac</th>
<th>H+</th>
<th>Lac-</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.75</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>0.75–x</td>
<td>+ x</td>
<td>0.25+ x</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Substitute and solve

• Ka = $[H^+][C_3H_5O_3^-] = 1.4 \times 10^{-4}$
  $[HC_3H_5O_3]$ 

• Ka = $(x)(0.25 + x) = 1.4 \times 10^{-4}$
  $(0.75 - x)$

• Since x is small

• Ka = $(x)(0.25) = 1.4 \times 10^{-4}$
  $(0.75)$

• $[H^+] = 4.2 \times 10^{-4}$ and pH = 3.38
Buffering capacity

• A weak solution of a buffer (low concentration) and a strong solution of a buffer (high concentration) will have the same pH (controlled by the dissociation).

• The concentrated buffer will have much more buffer capacity. It will resist changing pH when more acid or base is added.
Further example

• Calculate the pH and pH change that results from bubbling 0.010 mol HCl gas through 1.0 L of 5.0 M HAc and 5.0 M NaAc

• Use short cut of Henderson-Hasselbalch eqn

  pH = pKa + log ([Ac-]/[HAc])
  pH = -log(1.8x10^{-5}) + log (1)
  pH = 4.74 (before adding HCl)
Further example

• Major species: H+, Cl-, $\text{C}_2\text{H}_3\text{O}_2^-$, Na+, H$_2$O,

• Strong conjugate base so the new H+ from the HCl will form molecular $\text{HC}_2\text{H}_3\text{O}_2$. Assume this reaction will go to completion, as long as there is $\text{C}_2\text{H}_3\text{O}_2^-$

• Reaction of interest:

• $\text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \rightarrow \text{HC}_2\text{H}_3\text{O}_2$

  From HCl  From eqm  Can’t contribute to pH
Modified ICE table for stoich.

\[
\begin{array}{ccc}
 & H^+ & C_2H_3O_2^- & HC_2H_3O_2 \\
\text{Before} & 0.010 \text{ M} & 5.00 \text{ M} & 5.00 \text{ M} \\
\text{After} & 0 & 4.99 \text{ M} & 5.01 \text{ M} \\
\end{array}
\]

- pH = pKa + log \left( \frac{[A^-]}{[HA]} \right)
- pH = 4.74 + log \left( \frac{4.99}{5.01} \right) = 4.74 - 0.0017 \\
  \text{or 4.74  So the buffer consumed all added H} +}
Selecting a buffer system

• Sometimes a chemist needs a buffer for a specific pH.
• Buffers work best (highest buffer capacity when \([A^-] = [HA]\) or \([A^-]/[HA] = 1\)
  • so substitute this in the HH eqn
  • \(pH = pK_a + \log([A^-]/[HA])\) but this is 1 so..
  • \(pH = pK_a\) or as close as you can get.
Titrations

• Titration is the stepwise addition of a known concentration of acid or base into an unknown until the unknown is just consumed. This is usually observed by the change of an indicator.
Strong Acid/Strong Base

25.00 mL of 0.10 M HCl titrated with 0.10 M NaOH

Equivalence point $Na \times Va = Nb \times Vb$

Sharp curve break

pH at EQ pt = 7
Reading Titration graphs

25.00 mL of \(?\) M HCl titrated with 0.10 M NaOH

Vol = 12.50 mL
Reading Titration curves

• 12.50 mL x 0.10 N = 25.00 mL x ? N HCl?
• 0.05 N HCl
• HCl = 1 eq/mole so
• 0.05 M HCl is strength of unknown acid.
Strong Base titrated w acid.

25.00 mL of 0.10 M NaOH titrated with 0.10 M HCl
Titration of weak acid

25.0 mL of 0.10M Acetic acid $K_a=1.8 \times 10^{-5}$

Starting pH

Equivalence point

Starting pH

Equivalence point

Volume of Strong Base Added  0.10 M NaOH
Check for understanding

• Equivalence point is defined as
• $Na \times Va = Nb \times Vb$
• This is not typically $pH=7$ when dealing with weak acids!!!
• Why?
Comparison strong/weak acid

![Graph showing the comparison between strong and weak acids. The graph plots pH against mL of base added. The strong acid line is labeled with a blue diamond marker, while the weak acid line is labeled with a red triangle marker. The strong acid line shows a sharp pH increase at a lower base addition than the weak acid line.]
Weak acids/Strong Acids

- The weaker the acid the lower the $Ka$
- The lower the $Ka$
- The shallower the titration curve is
- Higher initial pH
- The more sloped the equivalence break point transition is.
Find the Equivalence Point
(Geometric method)

1) using a ruler, draw lines that follow the flat, more horizontal part of the curve

2) draw a line that follows the flat, more vertical part of the curve

Weak Acid Titration Curve

Buret Volume (mL)

pH
Find the Equivalence Point (Geometric method)

3) using a ruler, measure the distance between the top intersection and the bottom intersection

4) the geometric center of this line segment is the equivalence point
Find the Equivalence Point (Geometric method)

5) draw a vertical line from the equivalence point to the x-axis

6) where the line crosses the x-axis is the volume at the equivalence point (28.7 mL in this case)
Find the Mid Point (Geometric method)

1) if there is a steep rise in the pH at the beginning of the graph, draw a line that follows the steep part of the curve
Find the Mid Point (Geometric method)

2) using a ruler, measure the distance between the far left and right intersections

3) the geometric center between these points is the mid point
Find the Mid Point (Geometric method)

4) draw a horizontal line from the mid point to the y-axis

5) where the line crosses the y-axis is the pH at the equivalence point (pH = 7.2 in this case)
Finding Ka

• At mid-point, some thing miraculous happens

• $\text{pH}_{\text{mid}} = \text{pK}_a$

• So time for antilog \hspace{1cm} $10^{-\text{pK}_a} = \text{K}_a$

• $10^{-7.2} = \hspace{1cm} 6.31 \times 10^{-8}$
What are the $K_{a1}$, $K_{a2}$, and $K_{a3}$?

Titration curve of phosphoric acid, $H_3PO_4$. 

![Titration curve](image)
How close did you get?

$$\text{H}_3\text{PO}_4\text{(s)} + \text{H}_2\text{O}_\text{(l)} \rightleftharpoons \text{H}_3\text{O}^\text{+} (\text{aq}) + \text{H}_2\text{PO}_4^- (\text{aq}) \quad K_{a1} = 7.5 \times 10^{-3}$$

$$\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O}_\text{(l)} \rightleftharpoons \text{H}_3\text{O}^\text{+} (\text{aq}) + \text{HPO}_4^{2-} (\text{aq}) \quad K_{a2} = 6.2 \times 10^{-8}$$

$$\text{HPO}_4^{2-} (\text{aq}) + \text{H}_2\text{O}_\text{(l)} \rightleftharpoons \text{H}_3\text{O}^\text{+} (\text{aq}) + \text{PO}_4^{3-} (\text{aq}) \quad K_{a3} = 2.14 \times 10^{-13}$$