Acids and Bases IV

Revision: Henderson - Hasselbalch Equation

• For a buffer solution, which contains similar concentrations of a conjugate acid/base pair of a weak acid:

\[ K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{[H^+][\text{added base}]}{[\text{added acid}]} \]

since the dissociation of HA or protonation of A\(^-\) doesn’t lead to a significant change in the concentrations of these species.

Rearranging:

\[ \text{pH} \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]} \]
Buffers

- A solution containing both:
  - a weak acid + its salt.
  OR
  - a weak base + its salt.

withstands pH changes when (limited) amounts of acid or base are added.

- Reason: Le Châtelier’s principle.
  - if add acid, then reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ goes to left to absorb change;
  - vice-versa if add base
Buffers

- Solutions containing both a weak acid + its salt OR a weak base + its salt that withstand pH changes when (limited) amounts of acid or base are added.

\[
\text{Buffer after addition of } H_3O^+ \quad \text{Buffer with equal concentrations of conjugate base and acid} \quad \text{Buffer after addition of } OH^- \\
\begin{align*}
\text{CH}_3\text{COO}^- & \quad \text{CH}_3\text{COOH} \\
H_3O^+ & \quad \text{CH}_3\text{COO}^- \quad \text{CH}_3\text{COOH} \\
\end{align*}
\]

\[
H_2O + CH_3COOH \leftarrow H_3O^+ + CH_3COO^- \quad CH_3COOH + OH^- \rightarrow H_2O + CH_3COO^- 
\]
Example

• Find pH of solution which is 0.1 M in NH$_4^+$ and 0.2 M in NH$_3$ where p$K_a$ of NH$_4^+$ = 9.2

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

| before: | 0.2 | 0.1 | 0 |
| after: | 0.2 $- x$ | 0.1 $+ x$ | $x$ |

Using Henderson-Hasselbalch:
Effect of pH Change on Buffer

- Consider change in pH of pure water (pH = 7) if we add $10^{-3}$ M HCl:

  $$[H^+] = 10^{-3}\text{ M (can neglect amount already present in water)}, \text{ so pH goes from 7 to 3}$$

  Huge change!

  What about buffers?
Example

Consider a buffer solution with 0.1 M each of sodium acetate (NaA) & acetic acid (HA):

(found earlier that pH = 4.7)

What is the pH when $10^{-3}$ M HCl is added?

\[
\begin{align*}
\text{HA} & \rightleftharpoons \text{H}^+ + \text{A}^- \\
\text{initially:} & \quad 0.1 \quad 10^{-3} \quad 0.1 \\
\text{eqm:} & \quad 0.1 + 10^{-3} - x \quad x \quad 0.1 - 10^{-3} + x
\end{align*}
\]

i.e., suppose all but $x$ of the added H$^+$ → HA

but $x$ will be very small...
Using the Henderson-Hasselbalch Equation:

\[
pH \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]}
\]
Buffer Preparation and Capacity

Buffer Preparation

- If the pH of a required buffer is $pK_a$ of available acid then use equimolar amounts of acid and conjugate base.

- If the required pH differs from the $pK_a$ then use the Henderson-Hasselbalch equation.

Buffer Capacity

Buffer capacity is related to the amount of strong acid or base that can be added without causing significant pH change.

Depends on amount of acid & conjugate base in solution:

- highest when $[HA]$ and $[A^-]$ are large

- highest when $[HA] \approx [A^-]$ (most effective buffers have acid/base ratio less than 10 and more than 0.1 $\Rightarrow$ pH range is $\pm 1$)
Buffers in Natural Systems

• Biological systems, e.g. blood, contain buffers: pH control essential because biochemical reactions are very sensitive to pH

• Human blood is slightly basic, pH ≈ 7.39 – 7.45

• In a healthy person, blood pH is never more than 0.2 pH units from its average value

• pH < 7.2, “acidosis”; pH > 7.6, “alkalosis”

• Death if pH < 6.8 or > 7.8
Buffer System in Blood

• “Extracellular” buffer (outside cell)

\[ H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \]

\[ H_2CO_3 \rightleftharpoons H_2O + CO_2 (g) \]

– Removal of CO\(_2\) shifts equilibria to right, reducing [H\(^+\)], i.e., raising the pH

– The pH can be reduced by:

\[ H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \]
Another Blood Buffer

- Phosphate buffer, present inside cells ("intracellular" buffer)
- $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$:

$$
\text{H}_2\text{PO}_4^- \iff \text{H}^+ + \text{HPO}_4^{2-}
$$

from $\text{H}_3\text{PO}_4$, a tribasic (triprotic) acid

DEMO
Titrations

• **Equivalence Point:**
  - *when number of moles of added base = original number of moles of acid*
    - Strong acid/strong base $\text{pH} = 7$
    - Weak acid/strong base $\text{pH} > 7$
    - Strong acid/weak base $\text{pH} < 7$

• **End Point:**
  - *when a colour change in the indicator is observed*

$\Rightarrow$ Choose an indicator that changes colour close to the equivalence point
An Acid-base Titration

A  H^+(aq) + X^-(aq) + M^+(aq) + OH^-(aq)  \rightarrow  H_2O(l) + M^+(aq) + X^-(aq)  C
### Titrations: Strong Acid / Strong Base

**Equivalence Point at pH 7**

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<tr>
<th>Volume of NaOH added (mL)</th>
<th>pH</th>
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<tbody>
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<td>12.43</td>
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<tr>
<td>80.00</td>
<td>12.52</td>
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</tbody>
</table>

**Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH**

**Phenolphthalein**

pH = 7.00 at equivalence point

**Methyl red**
Titrations: Weak Acid / Strong Base

- equivalence point pH > 7 (value depends on starting concentrations)
- change is more gradual
Titrations:
Weak Base / Strong Acid

- equivalence point pH < 7
(value depends on starting concentrations)
Titrations:
Strong Base/Weak Acid

Titration of 40.00 mL of 0.1000 $M$ $H_2SO_3$ with 0.1000 $M$ NaOH

- $pK_a1 = 1.85$
- $K_a1 = 7.19$
- $[H_2SO_3] = [HSO_3^-]$ at first equivalence point
- $pH = 4.25$
- $[HSO_3^-] = [SO_3^{2-}]$ at second equivalence point
- $pH = 9.86$

Buffer region:

Volume of NaOH added (mL):

0 20 40 60 80 100