The pH of aqueous salt solutions

- Sometimes (most times), the salt of an acid-base neutralization reaction can influence the acid/base properties of water.

  - NaCl dissolved in water: pH = 7
  - NaC$_2$H$_3$O$_2$ dissolved in water: pH > 7 (basic)
  - NH$_4$Cl dissolved in water: pH < 7 (acidic)

- To determine whether a salt will make water acid, basic, or not influence the pH at all, we need to look at the type of reactions that make them.
The pH of aqueous salt solutions

• When an acid-base neutralization reaction occurs, a salt and water are produced:

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

NaCl in water = Na\text{ }^{+}_{(aq)} + \text{Cl}^{-}_{(aq)}

• The reaction above shows what happens when a strong acid and strong base react.

• The salt of a strong acid-strong base neutralization reaction has no acid/base properties (the resulting solution would have a pH of 7)

When a strong acid/strong base reacts with any other base/acid, reaction goes “all the way to the right”
The pH of aqueous salt solutions

- When a weak acid is reacted with a strong base, a salt and water are produced:

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}_{(aq)} \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l)
\]

- The resulting solution would be **basic** (pH > 7), even though a “neutralization reaction” has occurred.

If you made up a solution by dissolving NaC\(_2\)H\(_3\)O\(_2\) in water, the solution would be **basic**.
The pH of aqueous salt solutions

• When a strong acid and a weak base are reacted in a neutralization reaction, the resulting solution is *acidic* (pH < 7):

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

If you made up a solution by dissolving NH\(_4\)Cl in water, the solution would be *acidic*.
The pH of aqueous salt solutions

- Let’s look at why this is so…

1. **Salt of a strong acid and a strong base:**

   - Both the strong acid and strong base would ionize/dissociate completely if put in water

   
   \[ \text{HCl}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \]

   \[ \text{NaOH}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{OH}^-_{(aq)} \]

   - The one-way arrows here imply that the reverse reactions do not occur to any significant extent (\(\text{Cl}^-_{(aq)}\) is a really bad base and \(\text{Na}^+_{(aq)}\) is a really bad acid)

   The conjugate base of a strong acid has no base properties in water
   The conjugate acid of a strong base has no acid properties in water
The pH of aqueous salt solutions

- **Salt of a strong acid and a weak base:**
  \[
  \text{HCl}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4\text{Cl}_{(aq)}
  \]

- When \(\text{NH}_3\) (a weak base) is dissolved in water, an equilibrium results:
  \[
  \text{NH}_3_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}
  \]

- If \(\text{NH}_4^+\) is a weak acid, then when a salt containing \(\text{NH}_4^+\) (e.g. \(\text{NH}_4\text{Cl}\)) is dissolved in water, the resulting solution will be acidic.
The pH of aqueous salt solutions

• **Salt of a weak acid and a strong base:**
  \[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \]

• When \( \text{HC}_2\text{H}_3\text{O}_2 \) (a weak acid) is dissolved in water, an equilibrium results:
  \[ \text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(aq) \]

• If \( \text{C}_2\text{H}_3\text{O}_2^- \) is a weak base, then when a salt containing \( \text{C}_2\text{H}_3\text{O}_2^- \) (e.g. \( \text{NaC}_2\text{H}_3\text{O}_2 \)) is dissolved in water, the resulting solution will be basic.
Chemical equations for salt hydrolysis reactions

• You can recognize salts that will influence the pH of water from the positive and negative ions in the formula for the salt:

  \[\text{NaCl (Na}^+\text{, Cl}^-\text{)}\]

  \[\text{NaC}_2\text{H}_3\text{O}_2 \text{ (Na}^+, \text{C}_2\text{H}_3\text{O}_2^-\text{)}\]

  • KF (K\(^+\), F\(^-\))

  • NH\(_4\)Cl (NH\(_4\)^+, \text{Cl}^-)\]
Chemical equations for salt hydrolysis reactions

• The positive ion *might* be acidic and the negative ion *might* be basic.

\[ \text{positive ion} + \text{negative ion} \]

• NaCl (Na\(^+\), Cl\(^-\))
• NaC\(_2\)H\(_3\)O\(_2\) (Na\(^+\), C\(_2\)H\(_3\)O\(_2\)\(^-\))
• KF (K\(^+\), F\(^-\))
• NH\(_4\)Cl (NH\(_4\)\(^+\), Cl\(^-\))
Chemical equations for salt hydrolysis reactions

- If the cation (positive ion) of the salt is NH$_4^+$, dissolving the salt into water will produce an acidic solution.
- If the anion (negative ion) is the conjugate base of a weak acid, the salt will make the solution basic.
- Cases involving NH$_4^+$ with weak base anions won’t be considered.

The strong acids:
- Hydrochloric (HCl)
- Hydrobromic (HBr)
- Hydroiodic (HI)
- Nitric (HNO$_3$)
- Sulfuric (H$_2$SO$_4$)
- Chloric (HClO$_3$)
- Perchloric (HClO$_4$)

Conjugate bases:
- Cl$^-$
- Br$^-$
- I$^-$
- NO$_3^-$
- SO$_4^{2-}$
- ClO$_3^-$
- ClO$_4^-$

* Conjugate base of H$_2$SO$_4$ is HSO$_4^-$, but SO$_4^{2-}$ is not basic; HSO$_4^-$ is basic.
Chemical equations for salt hydrolysis reactions

• So, for example:
  – Will $\text{NH}_4\text{NO}_3$ make a solution acidic, basic, or have no effect?
  – $\text{NH}_4^+$ will make the solution acidic. $\text{NO}_3^-$ is the conjugate base of a strong acid ($\text{HNO}_3$), so it is not basic.
  – The resulting solution will be acidic, according to the following chemical equation:

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$$

$\text{NH}_4^+$ is acidic – a $\text{H}^+$ donor
Chemical equations for salt hydrolysis reactions

• Another example:
  – Will LiF make a solution acidic, basic, or neutral?
  – The cation isn’t NH$_4^+$, so it’s not acidic.
  – The anion is F$^-$. The conjugate acid is HF (not one of the strong acids, so F$^-$ is a weak base)

\[
F^- + H_2O \rightleftharpoons HF + OH^- \\
\]

F$^-$ is basic – a H$^+$ acceptor
Buffers are **mixtures of weak acid/conjugate base pairs** that are able to resist significant changes in pH when small quantities of acids or bases are added.

- They are particularly resistant to changes in pH, when small amounts of a strong acid or base is added.
- **Example**
  - When 0.02 mol of NaOH is added to 1L of water, the pH jumps from 7.0 to 12.3 (5.3 units)
  - When 0.02 mol of NaOH is added to 1L of 0.3 M HC₂H₃O₂/0.3 M NaC₂H₃O₂ buffer, the pH jumps just 0.06 units
Buffers in everyday life

- Because so many chemical reactions (including ones that occur in our body) produce/consume H\(^+\), pH regulation is essential
- Our blood is buffered (H\(_2\)CO\(_3\)/HCO\(_3^-\)/CO\(_3^{2-}\)) to a pH of 7.4.
- Many metabolic reactions produce H\(^+\) and CO\(_2\). pH is extremely important in cellular reaction (e.g. many enzymes will work only near pH = 7.4)
- The body needs to regulate pH within a narrow range (keep it very close to 7.4). Below pH = 6.8 and above pH = 7.8, cell death occurs
Buffers

How do buffers work?

- Since buffers contain both acid and base components, they are able to offset small quantities of another acid or base added to them.
  - The addition of an acid to a buffer consumes some of the base that is already present in the buffer.
Buffers

How do buffers work?

- Since buffers contain both acid and base components, they are able to offset small quantities of another acid or base added to them.

- The addition of a base consumes some of the acid that is already present in the buffer

\[
\text{Base} + \text{Buffer} \rightarrow \text{neutralization products}
\]
Buffers

• As an example, consider a buffer that is made up from the following weak acid/conjugate base pair:

• Acid = HF
• Conj. base = F\(^{-}\) (in the form of NaF)

Buffer mixture
Buffers

Addition of an acid to a buffer

• If HCl is added to this mixture, it will react with the base component of the buffer:

\[ H^+ + F^- \rightarrow HF \]

Remember, Cl\(^-\) (from HCl) has no influence on the pH of solutions, so it is not shown in this reaction.

Reaction of an acid with the buffer consumes a bit of the buffer’s base and makes more of the buffer’s acid.
Buffers

Addition of a base to a buffer

• If NaOH is added to this mixture, it will react with the acid component of the buffer:

\[
\text{OH}^- + \text{HF} \rightarrow \text{F}^- + \text{H}_2\text{O}
\]

Na\(^+\) (in NaOH) has no influence on pH, so it is not included in this reaction.

The reaction of a base with the buffer consumes a bit of the buffer’s acid and makes more of the buffer’s base.
The Henderson-Hasselbalch equation

i.e. THE BUFFER EQUATION

- The Henderson-Hasselbalch equation provides a means of calculating the pH of a buffer, provided the amounts of weak acid and conjugate base are known (or, more importantly, the ratio of their concentrations)

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

Buffer pH depends on 2 things:
- Concentration of weak base in buffer
- Concentration of weak acid in buffer

\(K_a\) is the acid ionization constant for the weak acid/base pair
THE BUFFER EQUATION

For example, a buffer is made up by adding 2.0 mol of HC$_2$H$_3$O$_2$ and 1.0 mol of NaC$_2$H$_3$O$_2$ to enough water to make up 1L of solution. If $K_a$ for HC$_2$H$_3$O$_2$ is $1.8 \times 10^{-5}$, what is the pH of the resulting solution?

\[
pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)
\]

Remember: $pK_a = -\log(K_a)$
THE BUFFER EQUATION

\[ \text{pH} = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

\[ \text{pH} = -\log(1.8 \times 10^{-5}) + \log \left( \frac{[1.0]}{[2.0]} \right) \]

\[ \text{pH} = 4.74 + (-0.30102999...) \]

\[ \text{pH} = 4.44 \]

log of a number that is less than 1 yields a negative answer
THE BUFFER EQUATION

- It can be seen that if the amounts of weak acid and conjugate base in the buffer are equal, the pH will be $pK_a$

\[
pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)
\]

$\log(1) = 0$ so $pH = pK_a$
THE BUFFER EQUATION

• This also provides a good way for you to check the pH that you’ve calculated for a buffer.

Remember, if \([A^-] = [HA]\) in the buffer, \(pH = pK_a\) for that buffer solution.

• If a buffer has more weak acid in it than weak base, the pH of the buffer will be less than \(pK_a\). (more acidic than \(pK_a\))
• If a buffer has more weak base in it than weak acid, the pH of the buffer will be greater than \(pK_a\). (more basic than \(pK_a\))
THE BUFFER EQUATION

- If a buffer contained 1000 times as much base as conjugate acid, the pH of the buffer would be $pK_a + 3$ (for the acetic acid/acetate buffer we just looked at, pH would be 7.74 (4.74 + 3))

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

<table>
<thead>
<tr>
<th>ratio</th>
<th>log(ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>-1</td>
</tr>
<tr>
<td>0.01</td>
<td>-2</td>
</tr>
<tr>
<td>0.001</td>
<td>-3</td>
</tr>
</tbody>
</table>
THE BUFFER EQUATION

Practice problem

1. What is the pH of a buffer that contains 0.090 mol NaC₂H₃O₂ and 0.010 mol HC₂H₃O₂ in 0.500 L?

   \[ K_a = 1.8 \times 10^{-5} \]

   \[ pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

   (Remember, the acid has one more H in its formula than its conjugate base)

2. Write the equation for the reaction that occurs when a strong acid is added to this buffer.

   *Hint:* it is easier to write represent a strong acid as “H⁺” and a strong base as “OH⁻” in these kinds of problems
The \( \text{H}_2\text{CO}_3/\text{HCO}_3^- \) buffer system

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

\[
\text{pH} = \text{p}K_a + \log\left( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \right)
\]

\[
\text{K}_a(\text{H}_2\text{CO}_3) = 4.3 \times 10^{-7}; \text{p}K_a = 6.37
\]

The lungs and the kidneys are key organs in maintaining acid-base balance in the body.
Electrolytes

- An electrolyte is a substance whose solution conducts electricity.
- Electrolytes produce ions (by dissociation of an ionic compound or ionization of an acid) in water. Salts are a typical example of an electrolyte.
- Non-electrolytes do not ionize when put into water. Glucose and isopropyl alcohol are examples of non-electrolytes.

Example of an electrolyte:

\[
\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)
\] (ions present in solution)

Example of a non-electrolyte:

\[
\text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(aq)
\] (no ions)
Electrolytes

• Some electrolytes are able to (essentially) completely ionize/dissociate in water.
  – Strong acids
  – Strong bases
  – Soluble salts

Example: \[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

• Some electrolytes produce equilibrium mixtures of ionized and non-ionized forms
  – Weak acids
  – Weak bases

Example: \[ \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^- \]
Electrolytes

- **non-electrolyte**: (ion concentration is ~zero)
- **weak electrolyte**: (ion concentration is low)
- **strong electrolyte**: (ion concentration is high)
Equivalents and milliequivalents

- One equivalent (1 Eq) is the molar amount of an ion that is needed to supply one mole of positive (or negative) charge.
- One mole of NaCl supplies
  - one mole of + charge ions (Na\(^+\))
  - one mole of – charge ions (Cl\(^-\))

Each of these is considered to be one equivalent (1 Eq)

Equivalents = moles of ion \times charge on ion

1 mole of Cl\(^-\) = 1 Eq
1 mole of Ca\(^{2+}\) = 2 Eq
1 mole of PO\(_4^{3-}\) = 3 Eq

Equivalents are units used like moles. They express the amount of ions (charge). Just like M (mol/L), concentrations can be expressed with equivalents, as Eq/L
Equivalents and milliequivalents

• Because the concentrations of ions in body fluids is usually low, the term, milliequivalents, is often seen.

\[
1 \text{ mEq} = 0.001 \text{ Eq} \\
1000 \text{ mEq} = 1 \text{ Eq}
\]
Equivalents and milliequivalents

- Example problem: the concentration of Na\(^+\) in blood is 141 mEq/L. How many moles of Na\(^+\) are present in 1 L of blood?

\[
1 \text{ mol Na}^+ = 1 \text{ Eq} = 1000 \text{ mEq}
\]

\[
(1L) \left( \frac{141\text{mEq}}{L} \right) \left( \frac{1\text{mol} \_ \text{Na}^+}{1000\text{mEq}} \right) = 0.141\text{mol} \_ \text{Na}^+
\]

- Volume of blood
- Concentration of Na\(^+\)
- Eq \(\rightarrow\) mol
Equivalents and milliequivalents

Another example: The concentration of Ca\(^{2+}\) ion present in a blood sample is found to be 4.3 mEq/L. How many mg of Ca\(^{2+}\) are present in 500 mL of blood?

\[
1 \text{ mol Ca}^{2+} = 2 \text{ Eq} = 2000 \text{ mEq}
\]

\[
(500 \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{4.3 \text{ mEq}}{L} \right) \left( \frac{1 \text{ mol Ca}^{2+}}{2000 \text{ mEq}} \right) \left( \frac{40.08 \text{ g Ca}^{2+}}{1 \text{ mol Ca}^{2+}} \right) \left( \frac{1000 \text{ mg}}{1 \text{ g}} \right) = 43 \text{ mg Ca}^{2+}
\]

volume of blood \(\rightarrow\) mL \(\rightarrow\) L

conc. of Ca\(^{2+}\) \(\rightarrow\) Eq \(\rightarrow\) mol

mol \(\rightarrow\) g \(\rightarrow\) mg
Acid-Base Titrations

Titrations are experiments in which two solutions are made to react together (a balanced equation for the reaction must be known).

In an acid-base titration, a known volume and concentration of base (or acid) is slowly added to a known volume of acid (or base).

An indicator is often used to find the endpoint in acid-base titration experiments.

Using $C_1V_1 = C_2V_2$, the concentration of the analyte can be determined (also need to consider coefficients).
Acid-Base Titrations

Before endpoint (acidic)

After endpoint (basic)
acid has been neutralized
Acid-Base Titrations

Know the concentration of this solution and can measure the volume needed to reach endpoint (example, this could be 0.100 M NaOH)

Know the volume of this solution, but not the concentration (example, this could be 25.00 mL of HNO₃)
Acid-Base Titrations

Example:
It takes 21.09 mL of 0.100 M NaOH to neutralize 25.00 mL of HNO₃. What is the concentration of HNO₃?

\[
\text{NaOH} + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}
\]

At endpoint:
\[
\text{# of moles of NaOH added} = \text{# of moles of HNO}_3
\]

\[
C_{\text{NaOH}} V_{\text{NaOH}} = C_{\text{HNO}_3} V_{\text{HNO}_3}
\]
Acid-Base Titrations

\[ C_{NaOH} V_{NaOH} = C_{HNO_3} V_{HNO_3} \]
\[(0.100M)(21.09mL) = C_{HNO_3}(25.00mL)\]
\[C_{HNO_3} = 0.08436M\]
\[C_{HNO_3} = 0.0844M\]
Acid-Base Titrations

• In a sulfuric acid-sodium hydroxide titration, 17.3 mL of 0.126 M NaOH is needed to neutralize 25.0 mL of H₂SO₄ of unknown concentration. Find the molarity of the H₂SO₄ solution.