pH and Buffers

Bob Hall, Laramie WY.
Goal of talk is **NOT** to teach everything you need to know about water and brewing. The below book will do that!

Rather I will cover some basic chemistry that will enable you to understand more advanced concepts.

These concepts seem simple, e.g., pH and buffering, yet (to me anyway), these ideas require some thought.
Water can dissociate

\[ H_2O \leftrightarrow H^+ + OH^- \]
\[ 2H_2O \leftrightarrow H_3O^+ + OH^- \]

In pure water \([H^+] = [OH^-]\) and the concentration is really low, \(10^{-7}\) moles / liter

A mole is \(6.02 \times 10^{23}\) atoms, molecules, ions, charge, etc. 1 liter contains 55 moles of water
Acids

$\text{H}_3\text{PO}_4 \rightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$  \hspace{1cm} \text{Phosphoric acid}

\[
\begin{align*}
\text{H} & \hspace{0.5cm} \text{O} \\
\text{H} & \hspace{1cm} \text{C} \hspace{0.5cm} \text{C} \hspace{0.5cm} \text{O} \hspace{-0.5cm} \text{H} & \rightarrow & \hspace{1cm} \text{H} & \hspace{0.5cm} \text{C} \hspace{0.5cm} \text{C} \hspace{0.5cm} \text{O}^- \\
\text{H} & \downarrow & & & \text{H} & \downarrow
\end{align*}
\]

\hspace{1cm} \text{Acetic acid}
Bases

NaOH $\rightarrow$ Na\(^+\) + OH\(^-\)

Sodium Hydroxide aka caustic
pH describes the concentration of H\(^+\) ions

\([H^+]\) can vary > 1 quadrillion! So need a good way to represent this variation

<table>
<thead>
<tr>
<th>Concentration</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-4}) mol/L</td>
<td>4</td>
</tr>
<tr>
<td>(10^{-7}) mol/L</td>
<td>7</td>
</tr>
<tr>
<td>(10^{-10}) mol/L</td>
<td>10</td>
</tr>
</tbody>
</table>

Technical definition: pH is negative logarithm of \([H^+]\)
Neutral

- Oven cleaner
- Household bleach
- Household ammonia
- Milk of magnesia
- Baking soda
- Seawater
- Human blood
- Pure water
- Milk
- Urine
- Black coffee
- Tomatoes
- Wine
- Vinegar, soft drinks, beer
- Lemon juice
- Stomach acid

Acidic

- Beer
- Mash
- Brewery caustic

This is pH of lambic!

Acid #5
Enzymes
Proteins that catalyze chemical reactions: i.e. they allow reactions to go faster by reducing the initial energy needed to start a chemical reaction.

Always end with ...ase

![Pyruvate Decarboxylase and Alcohol Dehydrogenase reactions](image)
A chain of amino acids
Forms a helix
Which folds in a certain way
And can merge with others
Enzymes are proteins with a physical structure specific to their function $\alpha$-amylase, with small starch molecule in the active site
(a) Interactions that determine the tertiary structure of proteins

- Hydrogen bond between side chain and carboxyl oxygen
- Hydrogen bond between two side chains
- Hydrophobic interactions (van der Waals interactions)
- Ionic bond
- Disulfide bond
pH determines how a protein folds, and structure determines function.
Enzymes have pH optima.

Chitinase from bacterium that lives in acidic pools

Chitinase from soil-dwelling bacterium
pH is a master variable in brewing

Controls starch conversion efficiency

Low pH (<5.8) reduces tannin extraction

Low pH allows proteins to clump in boil

pH affects flavor

See http://braukaiser.com/ for far more examples
Good news: Unless your water has high alkalinity, reasonable pH is easy to achieve.

\[ \alpha \text{ and } \beta \text{ amylases have optima at 5.6 and 5.3} \]

pH of 5.3 to 5.8 will work.
Measure pH with pH meter, ph strips, or indicator solutions

pH of my saison mash brewed last week
The big control of pH in mash and in your water: **buffers**

Substance that resists changes to pH when acid is added
The bicarbonate buffer

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

Carbon dioxide  Carbonic Acid  Bicarbonate
The relative amounts of bicarbonate and carbonic acid determine pH.
How does the buffer work?

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

Add some acid, reaction goes to the left.

But lots of \text{HCO}_3^- still remains, and pH stays the same, because lots of \text{HCO}_3^- means pH near 7
Some quick arithmetic to describe the effect of buffer

Imagine we have 0.003 mole $\text{HCO}_3^-$/liter of water. (Laramie water)

Add 0.001 moles of acid. That is enough to lower pH of pure water to 3. But if buffer is present, we still have 0.002 mole buffer/L. Only small change (about 0.5) to pH!

pH refresher: $0.001 = 10^{-3}$ \hspace{1cm} -log $10^{-3} = 3$
From pH and buffers to actually brewing. But first some definitions of what you read on a water report!

Alkalinity  Buffering capacity of water  Units mg CaCO$_3$ / Liter

Hardness  Concentration of Calcium and Magnesium  Units mg CaCO$_3$ / Liter.

Temporary Hardness  The component of hardness that can be reduced by boiling water.
Buffering in brewing (drinking) water
Called **Alkalinity**—units are mg CaCO₃ / L

**Alkalinity** is not the same as **alkaline!!!**

- Ability to resist change in pH when acid.
- **Acid Neutralizing Capacity**

- Having pH higher than 7. Does not really indicate alkalinity and is not as important for brewing.
Alkalinity

Measure by adding acid to water until the $\text{HCO}_3^-$ is exhausted, at pH $\sim 4.3$
High alkalinity brewing water is not good for brewing pale beers!

pH of mash can be too high, Subsequent pH in beer too high

How to lower alkalinity of brewing water:

Boil brewing water

Add acid (lactic, phosphoric)

Dilute with reverse osmosis (RO) water.
Boiling water reduces acid-neutralizing capacity

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightleftharpoons 2(\text{HCO}_3^-) + \text{Ca}^{2+} \]

Limestone, insoluble

Boiling drives off \( \text{CO}_2 \), reaction moves to the left. Limestone (chalk) settles on bottom and sides of pot. Reduces hardness also.

Does not work with sodium because \( \text{NaCO}_3 \) is soluble
Alkalinity of Laramie, WY water, December 2012

Preboil: 155 mg / L (as CaCO$_3$)

Post boil 105 mg / L—higher than the theoretical limit of about 60 mg /L
<table>
<thead>
<tr>
<th>Alkalinity (amount of buffering, ( \text{HCO}_3^- ))</th>
<th>Hardness (Ca and Mg)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>NaHCO(_3) can only reduce by acid or dilution. You live near my sister in MD. Sucks.</td>
<td>High CaSO(_4), like Burton water</td>
</tr>
<tr>
<td>High</td>
<td>Limestone water, can reduce by boiling and acid</td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>Pilsen type water, you live in Fort Collins, CO and are lucky</td>
<td></td>
</tr>
</tbody>
</table>
Mash is phosphate buffered

\[ \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \]

pH of mash with ion-free water is about 5.7
But brewing water has calcium which will lower mash pH because tricalcium phosphate is insoluble

$$3 \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 4\text{H}^+$$

Can add CaCl$_2$ or CaSO$_4$ to lower mash pH
Consider mash pH to be a tug of war between bicarbonate alkalinity, Ca\(^{2+}\) in brewing water and acidity of malt.

- **Ca\(^{2+}\) content in brewing water**
- **Alkalinity of brewing water**
  - Low
  - Mash pH
  - High

**Acidity of malt** (crystal, sark malts more acid)
Call this balance “Residual alkalinity”

Ca$^{2+}$ content in brewing water

Alkalinity of brewing water

low Residual Alkalinity high

Acidity of malt
From Brungard and AJ DeLange
The take home points

pH controls enzymes, enzymatic reactions (in part) make beer

Buffering controls and stabilizes pH. The bicarbonate buffer in water oppose the phosphate buffer in the mash

As Larry Horwitz says “These are broad targets”