The role of pH in brewing

pH is the measure of acidity which is the concentration of hydrogen ions H^+ in solution. Water naturally dissociates into its ionic components at a very low level to produce hydrogen ions H^+ and hydroxyl ions OH^-.

Water dissociates into its component ions

Understanding the factors

The ratio of the concentration of the products ($[H^+]$ and $[OH^-]$) to the concentration of the starting material (H_2O) is given by the equilibrium constant Kc which is expressed as:

$$Kc = \frac{[H^+(aq)]aqm \times [OH^-(aq)]aqm}{[H_2O\ (l)]aqm}$$

Since the concentration of water is constant, $[H_20\ (l)]aqm$ can be incorporated into a modified equation constant Kw, where:

$$Kw = [H^+(aq)]aqm \times [OH^-(aq)]aqm$$

Kw is called the concentration product of water and at 20°C (which is 298°Kelvin) Kw is equal to 10^{-14}. $mol^{-2}\ l^{-2}$. In pure water each water molecule dissociates to give to give one H^+ and one OH^- ion, hence at 20°C :

$$[H^+(aq)] = [OH^-(aq)]$$

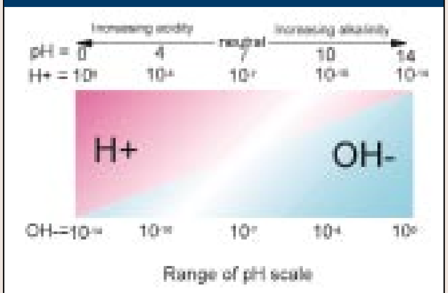
since $Kw = [H^+(aq)] \times [OH^-(aq)]$

then substituting for $[OH^-(aq)]$

$$Kw = 10^{-14} = [H^+(aq)]^2$$

$$[H^+(aq)] = 10^{-7}\ mol/l$$

FIGURE 1



Technical Summary 8

By Tim O'Rourke

Continuing this series of technical summaries for the Institute & Guild's AME candidates.

In 1909 the Danish Scientist Sorensen devised a simple numerical scale, the pH unit, which is the negative log_{10} of $[H^+]$. In a neutral solution where the $H^+ = 10^{-7}$ then the $-log_{10}10^{-7} = 7$, so the pH is 7.0 units.

With pH 7 as the neutral, then decreasing values from 7→ 0 means the concentration of H^+ ions increases and the solution becomes more acidic. Conversely as the pH value increases from 7 → 14 the levels of H^+ fall and the solution becomes less acidic or more alkaline. See Figure 1.

The negative log scale is also useful for measuring the hydroxyl ion $[OH^-]$ concentration:

$$pOH = -\ log_{10}\ [OH^-]$$

Knowing this, we obtain the following useful expression:

$$pH + pOH = -log_{10}\ K_W = 14.00$$

Since the pH scale is logarithmic, the intervals between each whole pH unit is not equivalent. pH units are usually given as mol/l which is also equivalent to µg/l and ppm. For simplicity the units will be shown as ppm. The effect of the logarithmic scale is shown in Table 1.

Measuring the acidity or pH of a wort and beer

Beer along with most beverages is acidic (i.e. with a pH below 7.0). Typical pH for the brewing operation for a standard lager is shown as follows:

Brewing water	pH 7.0	(neutral)
Mash	pH 5.6	±0.2
Boiled wort	pH 5.4	±0.2
At end fermentation	pH 4.0	±0.2

However as explained above the scale is logarithmic and hence the range of hydrogen ions H^+ is much greater for the finished beer than it is in the boiled wort.

- For wort with a pH of 5.4 ± 0.2 the range of ions H^+ concentration will be 4 ppm (2.5 ppm to 6.3 ppm)
- For the finished beer with pH 4.0 ± 0.2 the range of H^+ ion concentration will be 100 ppm (63 ppm to 159 ppm)

Controlling pH in the brewing process

The full range of pH is found in the brewing process are shown in Figure 2.

The fall in pH is governed by the mineral composition of the brewing water and mineral treatment added to the brewing water.

Increasing Acidity

The principal increase in acidity during mashing comes from the precipitation of phosphates and amino acids/polypeptides derived from the malt.

The phosphates dissociate:

1. $H_3PO_4 \rightarrow H^+\ H_2PO_4^-$
2. $H_2PO_{4-} \rightarrow H^+\ HPO_4^{2-}$

FIGURE 2

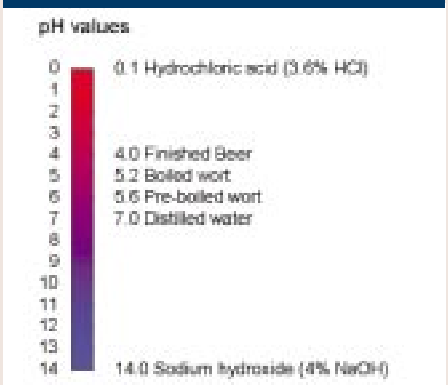


Table 1 - The relationship between pH and [H+] over the range pH 3.1 – 6.0.

pH	H^+ ppm	pH	H^+ ppm	pH	H^+ ppm
3.1	789	4.1	79.4	5.1	7.9
3.2	631	4.2	63.1	5.2	6.3
3.3	501	4.3	50.1	5.3	5.0
3.4	398	4.4	39.8	5.4	4.0
3.5	316	4.5	31.6	5.5	3.2
3.6	251	4.6	25.1	5.6	2.5
3.7	200	4.7	20.0	5.7	2.0
3.8	159	4.8	15.8	5.8	1.6
3.9	126	4.8	12.6	5.9	1.3
4.0	100	5.0	10.0	6.0	1.0

Ref: Taylor D. MBAA T.Q No4 1990.

Table 2 - The effect of the Mineral Composition of mash water on wort pH

Water composition	Wort pH	
	Before boil	After boil
50 ppm Ca^{2+}	5.5	5.4
50 ppm Ca^{2+} & 100 ppm CO_3^{2-}	5.8	5.6
350 ppm Ca^{2+}	5.1	5.0
350 ppm Ca^{2+} & 100 ppm CO_3^{2-}	5.4	5.3

Ref: Taylor D. MBAA T.Q No4 1990.

3. $HPO_4^{2-} \rightarrow 3H+\ PO_4^{3-}$

If calcium ions are present then the phosphates precipitate as calcium phosphate leaving $3H^+$ in solution, thus increasing the acidity.

4. $3Ca_2 + 2H_3PO_4^- \rightarrow 6H^+\ Ca_3(PO_4)_2\downarrow$

A similar reaction will occur with the amino acids and polypeptides present in the wort:

Amino Group-COOH $\rightarrow 2H^+$ + Ca(Amino Group-COO)$_2\downarrow$

When calcium sulphate ($CaSO_4$) is added to brewing water, the amino acids and phosphates form an insoluble salt (as shown above) leaving hydrogen ions (H^+) and sulphate ions (SO_4^{2-}) in solution. The increase in hydrogen ion concentration means that the solution becomes more acidic.

The change in mineral ion composition and precipitation of calcium salts account for most of the pH fall prior to fermentation. During fermentation the beer becomes more acidic (pH falls from around 5.2 to 4.0). A small amount of this fall will be due to further precipitation of calcium salts but the majority of the fall in pH is brought about by the excretion of organic acids by yeast.

Decreasing Acidity

However other mineral ions present in water can react to impede the fall in pH, and these are the salts of carbonates (CO_3) and bicarbonates (HCO_3) often called temporary hardness.

1. $Ca(HCO_3)_2 \rightarrow Ca^{2+} + 2HCO_3^-$

2. $2HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$

3. $H_2CO_3^- \rightarrow H_2O + CO_2\uparrow$

The production of hydroxyl ions (OH^-) "mops up" free hydrogen ions (H^+) to form water and hence limiting the fall in pH. It is therefore necessary to treat all brewing water to remove temporary hardness to ensure the correct fall in pH is achieved. The effect of the ionic composition on pH is shown in Table 2.

Temporary hardness is also responsible for scale and must be removed from process water such as boiler feed water, CIP water and water used in bottle washers, pasteurisers and bottle rinsers to avoid unnecessary scale build up.

Wort and beer as a buffer

Wort and beer are good buffers and are able to withstand small additions of acids or bases without significant changes in pH. Buffered solutions resist a change in pH when small amounts of acid or base are added.

Buffers contain acidic species to neutralise OH^- ions and a basic species to neutralise H^+ ions. However, these two species must be able to co-exist in a solution, without completely neutralising each other. For example beer is a weak acid (HX) and when it dissociates from its base (X) the following equilibrium occurs:

$$HX(aq) \leftrightarrow H^+(aq) + X^-(aq)$$

If OH^- ions are added they will remove H^+ ions to form water, thus increasing the pH. However, the equilibrium reaction will shift to the right as H^+ ions are released. The $[H^+]$ will therefore remain fairly constant, as will the pH. If more H^+ ions are added, then the above reaction will shift to the left.

The effect of changing concentrations on equilibria can be predicted using Le Chatelier's Principle. This principle states that if a system in equilibrium is disturbed then the equation moves in the direction which reduces the disturbance.

Hence in the system above, when more hydrogen ions are added the equilibrium will move towards production of HX in order to minimise the disturbance. This will cause the $[H^+]$ to decrease, to close to what it was before, and thus the pH will stay fairly constant.

The most effective buffering solutions are those which have similar concentrations of HX and X^-, because then the buffer has the capacity to absorb both acid and base, with the same effectiveness in either direction.

The effect of pH on the brewing process.

pH has a major effect on the rate of reaction, solubility and electrostatic charge of many molecules. This will have an important influence on beer quality and production throughout the brewing process:

- Physical e.g. colloidal stability of the beer
- Chemical e.g. isomerisation of alpha acid
- Enzymatic e.g. malt and yeast enzyme activity.

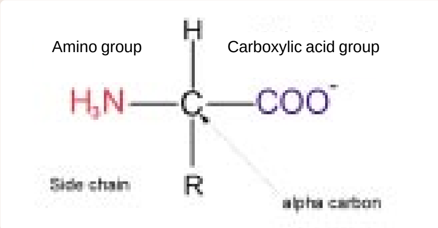
a. Physical

The solubility of inorganic ions such as mineral salt may be affected by the pH of the solution, especially if one or both of the ions are moderately acidic or basic. If a substance has a basic anion, such as $Mg(OH)_2$ and CaF_2, its solubility will be affected by the pH of the solution. In general the solubility of slightly soluble salts which contain basic anions, increase as the pH is lowered.

Most of the reactions in brewing are organic reactions in aqueous systems and these are effected by pH. Biological macromolecules act as acids and bases by donating and accepting protons. However, due to the size of these molecules, they often contain several different groups that accept or donate protons, thus having both acidic and basic groups rather than behaving as purely acids or bases.

These acidic and basic groups act as weak acids and bases. Changes in the pH around the macromolecule will determine which groups are protonated and which are not, which in turn determines properties of the molecule.

A typical example is amino acids, which are small molecules containing both an amino group and a carboxyl group. Since each amino group can be protonated and each carboxyl group de-protonated, the structure of an amino acid depends on the pH of the solution it is in. At pH 7, amino acids have the following structure:



When in an aqueous solution, amino acids can act as both acids and bases, i.e. they are amphoteric.

If only positive charges or only negative charges are present, the molecule is described as either a cation or an anion respectively. However, both positive and negative charges can be present at the same time. When this happens, the molecule is called a dipolar ion or zwitterion.

All amino acids exist as zwitterions at pH 7.0. There is no pH at which both groups are electrically neutral.

Amino acids can be joined together to form proteins and polypeptide molecules through condensation or dehydration reactions between the carboxyl group of one amino acid and the carboxyl group of the next. This bond is called a peptide bond.

It therefore follows that all the protein and polypeptide molecules in beer will be charged and this will effect physical properties such as their ability to coagulate and settle out as hot and cold break. Also their tendency to form hydrogen bonds leading to the formation of chill haze and foam.

Enzymes are complex proteins which rely on a three dimensional structure for their activity. Much of their structure is derived internal electrostatic bonding (e.g. hydrogen bonding) and hence they can only operate within a given pH range. (see later)

b. Chemical

There are a few non-enzyme catalysed chemical reactions which occur in brewing, examples are:

- Isomerisation of alpha acid into iso alpha acid during wort boiling. This is a basic chemical reaction, which is favoured by higher pH (pH 8 to 10) where it is goes to over 90% conversion. At wort pH (pH 5.2) typical conversions are around 60% in the kettle giving final bitterness utilisations of 40%.
  It is not practical to alter the pH of the wort, but many brewers chose to use pre-isomerised hop products, where the isomerisation of alpha acid is carried out at pH 8 for maximum conversion and the isomerised extract added to the wort.

- Colour is increased during wort boiling due to the Maillard reaction. This reaction is not favoured at lower pH thus limiting wort and hence beer colours.

- The husk of the malt contains polyphenols and silica compounds which are more easily extracted under alkaline (pH > 7.0) conditions. Polyphenols can produce a colloidal instability and astringency in the beer. Most of the polyphenols are extracted during the latter stages of sparging. It is important to ensure all brewing water is at least neutral or slightly acidic. Some brewers add mineral salts to all the brewing water including the sparge to maintain a lower pH thus avoiding this risk.

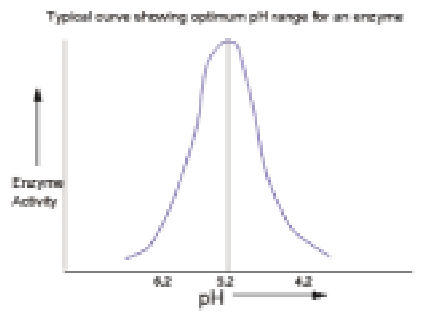
- An important reaction during maturation is the conversion of alpha-acetolactate excreted by the yeast into diacetyl in the fermenting beer. This is a natural decarboxylation reaction which occurs outside the yeast cell and the rate of decomposition is increased at lower pH. Many brewers acidify their wort to accelerate the reduction of acetolactate at the end of fermentation.

- At beer pH oxalates produced from the malt form insoluble salts with calcium ions and precipitate as calcium oxalate thus reducing the tendency for haze and gushing in packaged beer and beerstone production.

c.Enzymes

The majority of the chemical reactions in brewing are catalysed by enzymes. As was explained earlier these are made up of chains of amino acids and rely on a three dimensional structure for their activity. The charge on amino acids is critical to its structure and most enzymes will only work within defined pH ranges (see Figure 3).

Figure 3



The optimum pH ranges for the brewing enzymes fit well within the range of the typical mash pH (5.8 ± 0.2), thus:

- Alpha amylase which randomly hydrolyses starch – optimum pH 5.2

- Beta amylase which hydrolyses pairs of maltose sugar from non reducing end – optimum pH 5.5

- Proteases – hydrolyses proteins to polypeptides to amino acid – optimum pH 5.5

- Beta-glucanase hydrolyses beta glucans to reduce wort viscosity – optimum pH 6.0

As a result many of the process parameters which rely on efficient enzyme conversion will be affected by the pH of the wort, for example:

1. Proteolytic and amylolytic enzyme activity, which improves brewhouse extract.

2. Increases wort fermentability

3. Increases wort free amino and soluble nitrogen

4. Increases rate of mash tun run off

The other major contributor of enzymes is the yeast itself, which converts the sugars to alcohol through a complex series of enzymic reactions. The yeast as a living organism, is capable of regulating its own intracellular pH at around 6.5, but prefers to live in an acidic medium. It can tolerate pH as low as 2.0 for short periods of time, hence the use of acid washing.

Bacteria on the other hand generally do not like acidic conditions and only a specialised group of organisms can grow and infect beer. Few bacteria can tolerate the low pH conditions of acid washing. Lower beer pH is one of the essential properties of beer, which gives it microbial and physical stability.

Very acidic beers such as Belgian Lambic beers which have a pH around 3.5 are perceived as sharp and acidic, while beers with high pH are often described as soft and lacking in mouthfeel.

Summary

The role of pH is essential in beer production. It governs most of the physical and chemical reactions which occur and creates the necessary living environment for the yeast grow, flourish and complete the fermentation process.

The acidity of the beer itself contributes to the taste and character of the beer. Acid is one of the four principal tastes sensations and the pH will effect the way the other flavour compounds are perceived by the consumer. ■

Acknowledgement

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Further Reading

1. Moll "*Water*" in Brewing Science and Technology Series II published by the Institute of Brewing
2. O'Rourke "*Water*" in Brewing Science and Technology Series III (in print) published by the Institute and Guild of Brewing
3. O`Rourke "*Treatment and use of water in Brewing*" ***Brewers Guardian*** December 1998
4. Taylor D "*The importance of pH control during Brewing*" MBAA Technical Quarterly Vol 27 pp131 – 136.