# pHood pHenomena

Long ago, early cooks stumbled onto the effects of acid-base chemistry. And while at first the nuances of these reactions were mysterious, the concepts of pH control would soon affect and improve the taste, microbiological stability and even the texture of innumerable food products.

Chemists have explained these effects. In 1884, Svante Arrhenius defined acids as materials that release a proton or hydrogen ($H^+$), and bases as materials that donate a hydroxide ion ($OH^-$). In 1923, independent scientists Thomas Lowry and J. N. Brønsted stated that acids are materials that donate a proton, and bases are materials that accept a proton. In the same year, G. N. Lewis suggested that acids are electron-pair acceptors and bases are electron-pair donors.

The Brønsted-Lowry theory offers a broader definition than that of Arrhenius. It is, however, the modern interpretation of the Arrhenius concept — that an acid is a substance that, when dissolved in water, increases the hydrogen-ion concentration, and a base is a substance that, when dissolved in water, increases the hydroxide-ion concentration. This forms the foundation of the most-common system of quantifying acidity or alkalinity, called "pH."

### *Simple as pHalling off a log*

In solution, an acid dissociates to hydrogen ions and its conjugate base. Strong acids, such as hydrochloric (HCl) or sulfuric ($H_2SO_4$), will completely dissociate, yielding all of their hydrogen ions to the solution. Similarly, strong bases, like sodium hydroxide (NaOH) and potassium hydroxide (KOH), will completely ionize into hydroxide ions and a conjugate acid. When the concentrations of $H^+$ and $OH^-$ are equal, the solution is neutral. Increasing $H^+$ makes the solution acidic. Increasing $OH^-$ makes the solution alkaline.

Quantifying strength as a function of $H^+$ concentration is not simple, though, as the molarity (moles $H^+$ per liter of solution) could range from 0.01 to 0.00000000000001. Instead, we use a system developed in 1909 by Danish biochemist S.P.L. Sørensen, named "pH." Using a "p" to represent the German word for power, "potenz," the pH of a solution quantifies the power of hydrogen — defined as the negative of the logarithm

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of the molar hydrogen-ion concentration, or pH equals -log[$H^+$]. Using the pH scale, neutral solutions whose $H^+$ concentration measure $1x10^{-7}M$ are said to have a pH of 7. Solutions with pH ranging from 0 to 7 are acidic, and those ranging from 7 to 14 are basic. Solutions in which pH equals 1 are 10 times as acidic as pH equals 2.

While pH measures the $H^+$ in solution, percent titratable acidity (%TA) addresses all the hydrogen present, giving an actual percentage of acid. Calculating %TA takes the amount of a base needed to titrate an acidic solution to a pH of 7, and uses a formula to determine the percentage of acid.

Consider this illustration. Two beakers are filled with 100 ml of liquid. One contains 50 ml water and 50 ml hydrochloric acid (HCl), and the other contains 50 ml water and 50 ml sulfuric acid ($H_2SO_4$). The pH of the sulfuric acid solution will be lower, i.e. more acidic, as it yields two $H^+$ ions per molecule of acid versus the single $H^+$ in the hydrochloric. Both solutions will have a titratable acidity of 50%.

Another important value in the selection of acids is the dissociation constant, "Ka." The Ka indicates the amount of $H^+$ ions an acid gives up in solution. Acetic acid's Ka of 0.00001754 indicates little dissociation of $H^+$, making it a weak acid. Citric acid dissociates more completely, resulting in a Ka of 0.0074, making it a stronger acid. With as many as seven digits right of the decimal, some clever scientist decided to use the same strategy used for pH. Thus, we have pKa: the negative log of the dissociation constant. As with pH, lower pKa indicates stronger acid. For polyprotic acids, those that donate multiple $H^+$ ions, multiple pKa values exist. Citric acid, $H_3C_6H_5O_7$, and phosphoric acid, $H_3PO_4$, have three pKa values.

The strength of an acid — the amount needed to achieve a target pH — depends on the target pH itself. Acids become very weak when the target pH is lower than their pKa value. Acetic acid, with a pKa of 4.76, is very effective at lowering pH to 5.50, but not so much so when the target pH is 4.50.

### *pHood pHlavor*

Generally speaking, acids make foods taste sour. But all acids are not created equal. Type, level and product pH all affect the final level of sourness. With all other factors constant, decreased pH in a food will increase all acids' sourness. The rate of increase is not linear, though, resulting in variation of relative sourness across the pH spectrum. When pH is 3.0, malic acid will deliver far more perceived sourness than citric acid (per unit weight). As pH increases to 4.7, both acids yield about the same level of sourness. The key word here is "level," as switching these acids at a pH of 4.7 will not result in the same overall "flavor."

Citric and tartaric acids, being more hydrophilic than other food acids, impart a sourness that dissipates quickly. Their rapid dissipation gives these acids a clean, bright flavor effect, often a benefit in beverage applications. Sourness from less-hydrophilic acids, like acetic, fumaric and malic, will persist, and this allows developers to balance the taste of high-intensity sweeteners with sourness.

Beyond sourness, acids' flavor characters vary. Citric acid, the most widely used food acid in today's food and beverage industries, provides a sharp, yet clean and refreshing, tart taste. Acetic acid has a very volatile, pungent flavor, often lending the aroma of vinegar. The refreshing sourness of green apples comes from malic acid. In fact, all fruits (except tamarinds, which are actually seedpods) contain some malic acid, often blending with other acids to create the unique taste of each fruit. Malic offers a smooth lingering tartness. Fermentation of malic acid yields lactic acid — with its lingering mild taste, and subtle dairy aroma. Malolactic fermentation in wine results in a more-rich, buttery taste, versus the fresh fruity taste of malic acid. Tartaric acid lends a more-sharp taste than the other acids and is responsible for the distinctively hard taste of tamarinds. Fumaric is derived from malic acid. It is the strongest of the organic acids, with a taste that is clean and persistent, and it has a unique dryness.

### *pHight the power*

Buffers are substances that resist change in pH. They typically are comprised of a weak acid and its conjugate base — citric acid and sodium citrate, for example. Because it can supply $H^+$ ions or $OH^-$ ions, the buffer solution's pH remains fairly constant, despite the addition of limited quantities of strong acids or bases. By reducing large shifts in pH, buffers can provide improved stability of flavor, color, gelation rate and subsequent gel strength, and pH-sensitive sweeteners. Flavor characteristics can vary at different pH values (similar to the way colors can shift in different pH ranges). Also, the products can degrade and/or be lost at a pH level outside of the "optimum range." For example, the optimum pH for aspartame is 4.2.

"Buffer capacity" is measured in equivalents of acid (or base) that change the pH of one liter of solution by one pH unit. Buffer capacity is greatest at the pKa. It is inversely proportional to molecular weight. Low-molecular-weight acids, like acetic, which is 60 amu, will exhibit far greater buffering capacity than heavier acids like citric, which is 192 amu. This is true at each acid's pKa. Citric's buffering capacity is greater than acetic's at pH levels greater than 5.5, far above its first two pKa values.

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Dry mixes for instant beverages present an interesting application for buffers, as the water used for hydrating the beverages can vary in pH. Maintaining a specific pH range will better ensure consistent flavor of the product regardless of the water used. Other liquid systems can utilize buffers to keep pH in the range where preservatives are most effective. Citrate salts, for example, can help maintain a pH range of 3.0 to 4.5 — an ideal environment for benzoates. Typical usage levels for citrates range from 5% to 25% of the citric acid used. In this example, the buffer indirectly affects the taste. By eliminating swings in pH from variations in water pH, the flavor characteristics of the acidifiers and flavors used will be the same for people using all kinds of water.

And in some instances, buffers can directly influence flavor. At a given pH, a buffer will have a more- or less-sour taste impact. For example, PURAC, Lincolnshire, IL notes that at pH of less than 4, lactic acid buffers are more-sour than citric ones, which can help improve sourness in low pH items, such as candies.

### *Hea"pH"y metals*

Another means by which acids protect a food system is chelation. From the Greek word for "claw," chelators grab metal ions and form a ring around them. Chelated metal ions cannot participate in their normal reactions, such as precipitation, color formation or catalysis of oxidation. Chelation that forms a stable and water-soluble product is referred to as sequestration.

Of the acids commonly used for food applications, citric is the strongest chelator. Other acids that exhibit some chelating activity included tartaric, malic and lactic.

### *pHood SapHety*

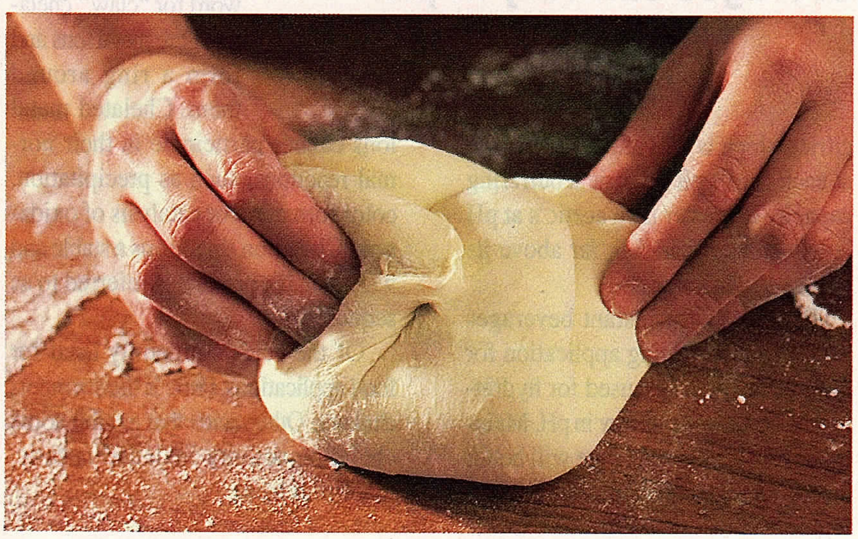
Controlling pH can provide bacteriostatic (inhibiting) or a bacteriocidal (killing) effects to improve foods' microbial stability. According to federal regulations, low-acid foods — those acidified to a pH of 4.6 or lower by the addition of acid or acid foods — are considered "acidified foods." As with flavor, all acids do not exhibit the same antimicrobial effects. Lactic is the most effective acid for controlling lactic-acid bacteria. Acetic acid is a better general inhibiting agent for yeasts and molds. In fact, the inhibitory effect of an acid depends not only on the type of acid used, but also on its dissociation constant, its usage level and the pH of the system to which it is added.

Acidification is especially important in canned products. The absence of oxygen, low acidity and abundance of water and nutrients all provide an ideal environment for the growth and reproduction of *Clostridium botulinum*. Acidification to a pH at or below 4.6, using Good Manufacturing Practices (GMPs), assures the inhibition of *C. botulinum* growth.

**Chemical leavening is achieved by chemical reactions between an acid and a base. Selection of a leavening acid requires consideration of two factors: dough rate of reaction and neutralizing value.**

So why not simply add enough acid to kill everything in a product? Because while pH levels in the neighborhood of 2.0 to 2.4 might destroy bacteria, they'll also offend consumers with overwhelming sour or tart tastes. In addition, over-acidification might cause problems with pH-dependant colorants and precipitation.

Using acids in combination can give developers some extra room when formulating to a given pH. Acetic acid is common in dressings and sauces — to inhibit growth of the spoilage indicator *Lactobacillus plantarum* — at levels around 2.0%. Lactic acid can be used at 2.5% to provide the same inhibitory effect, with a milder flavor than acetic. Using the two together allows for a reduction in total acid to 1.5%, or an increase in the total acidity, without creating an undesirable flavor effect in products that should taste less acidic, such as a cream sauce.



### *Don't be left pHlat*

Leavening, the production of gas that makes baked products rise, can be achieved either by yeast fermentation or through chemical reactions. The latter provides more-rapid and -consistent gas formation that allows processors a greater level of control. Thermal degradation of a compound, such as ammonium bicarbonate, yields carbon dioxide gas. Unfortunately, high-moisture, non-porous products can trap residual ammonia, resulting in off-flavor and color. Reacting an acid and a base under hot, moist conditions generates gas production.

Sodium bicarbonate is the typical base-reactant in these systems. Potassium bicarbonate can be substituted if reduced sodium is a concern. It requires up to 20% greater usage levels than the sodium counterpart, and can yield sharp aftertastes due to elevated pH in the finished product.

Selection of a leavening acid requires consideration of two factors. Dough rate of reaction (DRR) tells how quickly carbon dioxide is generated under processing conditions. This helps developers ensure the right timing of gas formation. Neutralizing value (NV) is a measure of acidity, indicating the amount of acid needed to neutralize 100 lbs. of sodium bicarbonate. Although a neutral endpoint is generally desired, excess acid or base may be added to compensate for pH-affecting additions to the dough, such as acidic fruit or buttermilk.

Adjustments to pH might also modify other factors of the finished product. For example, elevating the pH slightly, 8.0 to 8.5, will enhance chocolate's flavor impact. Similar increases in alkalinity have been shown to improve texture and volume.

### *pHirming up textures*

High methoxyl (HM) pectins, used for jams, jellies and a myriad of fruit preparations, require a soluble-solids level of 55% or higher and a pH ranging from 1.0 to 3.5 to gel. At a pH greater than 3.5, HM pectins will not gel, but can provide some viscosity. Gelation of low methoxyl (LM) pectins will occur at pH levels from 1.0 to 7.0 and higher if calcium is present. LM pectin gels are typically spreadable, with rigidity increasing as pH falls below the pKa of 3.5. Below the pKa, less dissociation of $H^+$ results in greater hydrogen bonding of the pectin chains, giving a more-rigid gel. Above the pKa, more acid groups are ionized, allowing for more cross-linking by calcium, creating a more-spreadable network.

System pH will also affect the gelation rate of HM pectins, based on the pectin's degree of esterification (DE). HM pectins, by definition, have greater than 50% DE. Below a 70% DE are the slow-set pectins, which reach their peak gel strength when pH is 3.05 to 3.15. DE values in the 70s indicate rapid-set pectins, whose firmness peaks at pH 3.35 to 3.45.

The effects of pH are somewhat different for gelatin gels. For these wiggly-jiggly treats, adding acids creates tartness and enhances the fruity flavors of the finished dessert. Adipic and furmaric acids typically are selected for these products because of their high acidity and low hygroscopicity. Using buffer salts, such as sodium citrate, helps protect the gelatin from degradation by low pH at high processing temperatures.

Water gels can be prepared using other hydrocolloids, such as carrageenan or carrageenan plus locust bean gum. Although the combination of carrageenan plus locust bean gum is relatively acid stable, carrageenan can undergo some acid hydrolysis at processing temperatures. As with gelatin, citrates are often used to buffer and protect the gum(s) until after gelation has occurred.

Coagulation of milk proteins into cheese has long used lactic-acid-producing cultures to drive the pH downward. More recently, processors have turned to direct acidification to shorten production times, increase coagulation consistency and improve control of pH development. Formulators can use lactic or acetic acids — as well as lemon syrup and vinegar — when making Ricotta cheese. Mozzarella cheese has been made using vinegar, 0.03%, added prior to renneting. Glacial acetic acid has been added to milk at about 2.7% in the preparation of *queso blanco* cheese.

### *Off the hoopH*

Meat processors steer pH in different directions depending on the type of product they are manufacturing. At slaughter, lactic acid begins building up in muscle tissues, driving the pH downward from near neutrality, 6.8 to 7.2. Slowly, pH approaches the isoelectric point — the pH at which the number of negative charges (alkaline) equals the number of positive charges (acid). This is the point of minimum water-holding capacity. Addition of alkaline phosphates pushes the pH of the meat upward — away from the isoelectric point, thus unfolding the proteins and creating space as well as binding sites in which water can reside.

Sodium tripolyphosphate is the most commonly used product in this application, which USDA limits to a 0.50% (finished basis) usage level.

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Cured-color development is favored by acid conditions. Studies have shown that lowering pH by 0.2 units can double the rate of cured-color formation. For this reason, combining phosphates, such as sodium tripolyphosphate (alkaline) with sodium acid pyrophosphate (acid) can provide an advantage, improving color development without sacrificing protein-extraction properties.

In dry and semi-dry sausage production, pH near the isoelectric point helps drive moisture out of the meat. As in the cheese industry, lactic-acid-producing cultures have been employed to gradually reduce pH through long fermentation cycles. Encapsulated citric acid can provide acid development that is more rapid than fermentation, yet controlled enough to avoid rapid pH reduction and subsequent product degradation.

***Less pHamiliar pHaces***

Glucono-delta-lactone, GDL, is technically not an acid. It's a carbohydrate that slowly hydrolyzes to gluconic acid and delta and gamma lactones. Slowly is the key word here: two hours at room temperature (25°C), less time as temperature increases. This slow acidification is complemented by a minimal effect on flavor. It can lower pH as effectively as other acids, without imparting sourness. "The low flavor perception of GDL makes it ideal where a lower pH is desired without imparting sourness," suggests John Fenstermacher, senior market development specialist, PURAC. "This is particularly applicable to refrigerated foods, fillings, sauces and dressings, and some prepared foods typically not associated with acid, such as mashed potatoes."

GDL's slow acidification has also been used to replace traditional fermentation processes for manufacture of cottage, feta and mozzarella cheeses, as well as yogurt. In both systems, processing time is reduced, with potential enhancements to taste, texture and yield.

Manufacturers of deli salads are more frequently targeting very low pH levels to increase shelf life. With such elevated acid levels, flavor becomes sour, even when combined with mild-tasting acids, like lactic. Fenstermacher offers GDL, incorporated into the salad at 0.20% to 0.50%, as a tool for obtaining the desired pH while improving the shelf life, but without harming the eating quality.

Sodium acid sulfate is a recently patented acidulant for food applications. With an acid strength similar to phosphoric acid (pKa 1.99), sodium acid sulfate acts as an effective acidulant, yet it exhibits sour-flavor intensity less than citric, malic and phosphoric acids. "The ability to obtain lower pH with reduced sourness allows for hot-filling items that typically require retorting," notes Carl Knueven, corporate manager, product development, Jones-Hamilton Co., Walbridge, OH. "Vegetables in a canned soup that is hot-filled will maintain a more-fresh texture," he continues, "rather than becoming soft and mushy through retorting." Usage levels will vary from 0.05% to 0.50% for highly buffered systems.

Product developers can also use sodium acid sulfate in conjunction with other acids to affect pH independent of flavor. One example is low-carb bagels that contain high levels of soy protein, which buffers the product's pH. Because mold inhibitors require pH less than 5.5, formulators often add high levels of acetic acid, yielding an overly sour taste. Knueven suggests that developers can create the desired taste with acetic acid, and then drive the pH to the necessary level using sodium acid sulfate.

It's difficult to imagine something so simple as hydrogen ions can affect so many facets of so many food systems. As developers, we need to be ever-watchful of how we maintain both "pHorm" and "pHunction" in the products we create. ■

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