Notes on acid adjustments:

In general, acidity levels in 2018 were lower than normal.

Grape acidity is critical for the winemaking process, as well as the quality of the wine.
There are 2 common ways to measure acidity pH and titratable acidity (TA).

An acid is a molecule that dissociates or ionizes in solution to yield a positively charged hydrogen ion (H^+) and a negatively charged ion. A solution's pH is a measure of the concentration of free hydrogen ions in solution. The more acid there is in juice or wine or the more you add, the lower the pH.
When acids ionize they release one or more H+ ions, the remaining portion then carries a negative charge because it has lost its H+ ion. Only a portion of the acids in wine are ionized, therefore some of acids remain in the un-ionized form. So, pH also measures the degree of ionization of the acids in grapes or wine.
The thing to remember about pH is that the higher the pH, the lower the acidity, and the lower the pH, the higher the acidity.

TA (titratable acidity), by comparison, is a measure of the concentration of acids in grapes, juice, must or wine. This includes both the H+ ions and un-ionized portion, as determined by titration, which involves adding enough of a basic compound such as Sodium Hydroxide (NaOH) to neutralize all of hydrogen ions. TA is largely responsible for a wine's tartness.

A **salt** is a chemical substance produced by the reaction when and **acid** with a **base** are combined in water. A salt consists of a positively charged ion (a cation), and a negatively charged ion (an anion). For example, when hydrochloric acid (HCL), is added to water, it separates into two charged ions (H^+ and CL^-). The H^+ ions cause the pH to drop, making the solution acidic. By comparison, when sodium hydroxide (NaOH), a base, is added to water, it separates into 2 charged ions—Na+ (a cation) and OH^- (an anion). The OH^- ion makes the solution basic—the opposite of acidic. When combined, the two chemicals react, forming (NaCL (table salt) and water (H_2O or (H+ OH^-). In doing so, both the acid and the base are neutralized.

Acidity varies throughout the season as the berries ripen. As grapes ripen, acidity decreases: pH goes up and TA goes down. Major influences include climate, weather events, farming practices, such as trellising, canopy management, irrigation, etc., soil characteristics, and topography, drainage, and exposure to sunlight. And of course, the longer you wait to pick, the lower the acidity. Acid levels vary widely in the same vineyard and even the same vines from year to year. So it's hard to predict what the levels will be when you harvest.
The bottom line is that acids levels can be too high or too low to make a balanced, stable wine.

The most common problem with wine grapes is low acidity, so it's prudent to adjust the acidity upward early in the winemaking process.

pH of grape juice/must influences:

- aroma and taste, color and balance of the wine
- malolactic fermentation
- how much SO_2 is needed to protect against oxidation
- susceptibility to bacterial spoilage
- how pH changes (goes up or down) as tartrates precipitate from solution.

Which is more important, pH or TA? Both are important, TA influences balance, a wine with low TA tastes flat, and a wine with high TA tastes sharp or tart. pH, though, influences aroma/taste, and color. It also determines stability of grape juice during cold soak, fermentation, MLF, during storage, and after bottling. So, make sure the pH level is within an acceptable range

For accuracy acidity should be measured after pressing and settling for white grapes. For red grapes allow at least 24 hrs. of skin contact. Repeat after pressing. When grape acidity falls outside the acceptable range adjustment should be made.

What is the acceptable range for grapes?

- TA: white: 6 to 9 g/L pH:.>3.1 but < 3.54
- TA: red: 5 to 8 g/L pH: >3.4 but <3.6

What is the acceptable range for wine?

- TA: white 6.5 – 8.5g/L pH: 3.2 to 3.3
- TA: red 6 up to 7 pH: >3.5 to <3.85

(higher pH will take more TA The optimal time to adjust juice is before fermentation, and the optimal range for white grapes is 3.2 to 3.3 and 3.4 to 3.5 for reds, regardless of TA!

Acidity will change naturally during winemaking:

- pH ↑ 0.2 pH units (during skin contact) less for whites, and 0.1 to 0.2 units (during fermentation), and 0.2 pH units during MLF, pH ↓ cold storage
- TA ↓ 1g/L fermentation, 1g/L or more during MLF
- TA ↓ cold storage/stabilization, little change in pH
- The bottom line is that if your juice has low acidity, it will be even lower when the wine if finished. That could be a problem.

There are 4 acidity conditions:

- **Moderate and ideal**: Moderate pH (3.0-3.5) and moderate TA 6-9g/L)
- **Low**: Low pH and high TA (pH <3.0 and TA >9g/L)
- **High**: High pH and low TA (pH >3.5 and TA <6g/L) (common in warm areas, and with extended hang-time)
- **Problematic**: High pH and high TA (pH >3.5 and TA >9g/L). This may be the result of high Malic acid, but this condition is fairly rare in California. It is usually the result of excessive Tartrate and excess Potassium ions. Such wines may resist adjustment and you may need to seek technical advice. High Malate is best remedied in the vineyard.

High TA (greater than 10.5 is usually the result of too much Malic acid. You'll need to do a 'double salt' treatment. Consult with Scott Labs or Vinequiry Enartis.

What to do:

- For low acidity juice — pH (>3.5) and low TA (< 6g/L) add Tartaric acid
- For high acidity juice— pH (≤3.0) and high TA (≤ 9g/L) add Potassium Bicarbonate
- For high pH juice(> 3.65) and moderately high TA (≤ 9g/L) add Tartaric acid.
  - Until pH drops to less than 3.65, TA will increase with the addition of tartaric acid – probably not what you wanted! However once pH drops to less than 3.65 (which it will if you add enough acid) the TA will begin dropping due to the Potassium Bitartrate formation.
- For mod. high pH (>3.5) and high TA (>10g/L) add $CaCO_3$. TA will come down but pH will not change much
- Wines with TAs above 10.5 g/L usually have excessive malic Acid and deacidification requires a double salt treatment
- Symbols: < (less than), ≤ (less than or equal to), > (greater than), ≥ (greater than or equal to).

Adjusting TA

- The best time to make adjustment is at the juice stage. Small changes can be made later, but try to do shortly after fermentation or MLF
- If TA is less than 6g/L — add Tartaric acid:
  - 1g/L of tartaric acid will increase TA by 1g/L.
  - 1g/L of tartaric acid will lower pH by roughly 0.1 pH unit, if adjusted pH is <3.65
- If TA is > 9g/L — add Potassium Bicarbonate:
  - 0.9 g/L will lower TA by 1g/L
  - 0.9 pH may increase by as much as 0.2 pH units, if adjusted pH is <3.65

What's the ideal pH range for red must?

- reds grapes: 3.4 to 3.5, regardless of TA
- If nothing else, get the pH within recommended range before fermentation.
- Later adjustments can result in tartrate instability problems particularly if it occurs after cold stabilization

The resulting pH after making an adjustment is an important consideration.

- below pH 3.65: pH↓ and TA↓
- above 3.65: pH ↑and TA↓

How tartaric acid behaves in solution: (a schematic representation)
Equilibrium in the reaction will depends on pH:

$$H_2Ta \leftrightarrow HTa^- + H^+ \leftrightarrow 2H^+ + Ta^{2-}$$

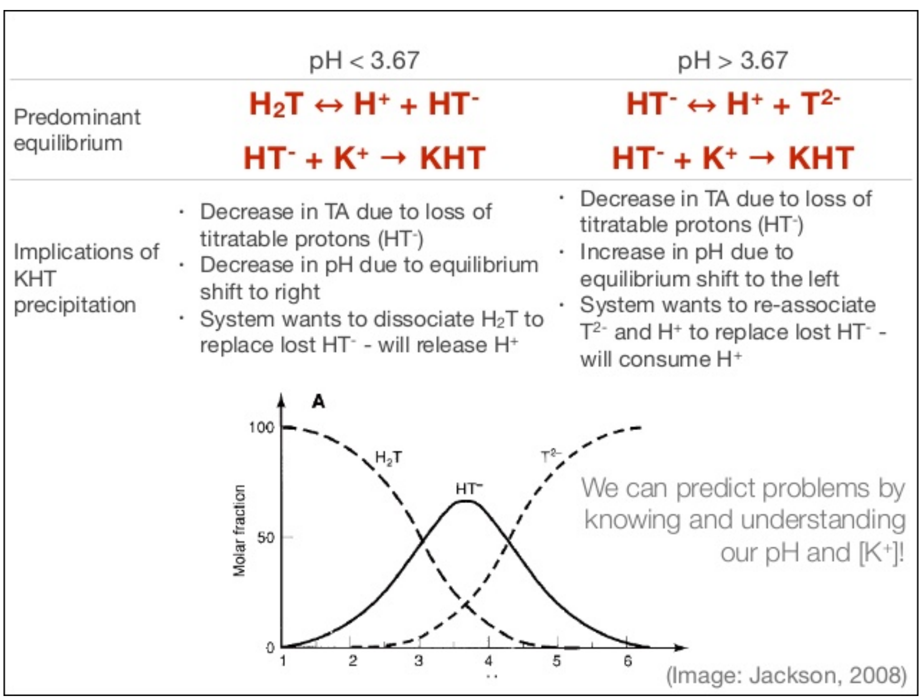
- **↔** represents constant equilibrium depending on pH
- **H_2Ta** (tartaric acid),
- **HTa^-** (is a Bitartrate ion), and
- **Ta^{2-}** (is a Tartrate ion)

Tartaric acid has two acid (-COOH) groups, that can lose their terminal hydrogen in solution. Since Tartaric acid has two H^+ ions that can be released in solution, depending on pH. There are 2 dissociation equilibria known as (pKa's). Stay with me here, I know it's a bit over the top, but it's an important concept. It's probably more than you need to know, but it helps to understand the process of acid adjustment:

- The pKa of an acid is the pH value when 50% of the acid is disassociated or ionized.
- Chemists use the concept of pKa to indicate an acid's strength, and each acid's pKa value(s) is a measure of the degree to which each acid ionizes.
- So the higher the pKa, the less ionized the acid is at typical wine pH values.
- As you would expect, pH goes as you add more acid.
- Tartaric acid has 2 pKa values, one occurs at about pH 3.0, and the other at about pH 4.25.

Equation 1. **$H_2Ta \leftrightarrow H^+ + HTa^-$** ($HTa^-$ predominates at pH ~3.0 to ~3.65: (pKa = 3.04). Some researchers use 3.67 instead of 3.65

Equation 2: **$H + HTa^- \leftrightarrow 2H^+ + Ta^{2-}$** ($Ta^{-2}$ predominates at pH 4.25 (pKa = 4.25)



*Note: In the graphic above, the author uses **T** rather than **Ta** to represent Tartaric acid and used pH 3.67 rather than 3.65 as peak of the Bitartrate curve, (probably used a different calculation method.*

The reaction of Tartaric acid in grape juice or wine at <u>normal</u> pH

$H_2Ta \leftrightarrow HTa^- + H^+ + K^+ \rightarrow KHTa + H^+$ (**K^+** represents a Potassium ion), KHTa represents Potassium Bitartrate, an insoluble salt that crystalizes out of solution, eliminating some Tartaric acid, and by doing so, reduces TA.

When pH is very high, say 4.0, there are relatively few Bitartrate ions to precipitate, mostly Tartrate ions. If you lower pH to say 3.85 by adding acid, there will be more Bitartrate ions to precipitate, so when this happens, TA drops but pH increases. Why you ask? The reason pH increases is that when pH is above 3.65, the equation shifts left ← from Tartrate ions **(equation 2)** to replenish some of the Bitartrate ions to maintain equilibrium:

$H^+ + HTa^- \leftarrow 2H^+ + Ta^{2-}$ (Note that there is a net loss of 1H+, that means pH goes up)

However, if you continue to add more tartaric acid pH will drop. Once it reaches 3.65, the point of maximum Bitartrate precipitation) or below, most of the dissociated ions will be Bitrate ions. As KHTa precipitate from solution, the equilibrium shifts to the right → **(equation 1** to replenish some of the Bitartrate ions lost to crystallization.

$H_2Ta \rightarrow H^+ + HTa^- + K^+ \rightarrow \downarrow KHTa + H^+$ (Note that when equilibrium shifts left, there is the release of 1H+, so pH goes down)

K_2CO_3 works to de-acidify low acid wines:

- by converting CO_3 to CO_2 (gas bubbles) and H_2O, neutralizing H+, pH goes up↑
- and the K+ ions combine with Bitartrate precipitates and TA goes down ↓
- below pH 3.65, the ppt. of KHTA caused pH to go down↓

$K_2CO_3 \rightarrow 2K^+ + CO_3^{-2} + HTa^-$ (in the juice of wine) $\leftrightarrow KHTa\downarrow + CO_3^{-2} + 2H^+ \rightarrow H_2O + CO_2$ bubbles.

What's the best approach to make adjustments?

- First measure careful and determine where you want to be?
- two options:

Bench trials: how much Tartaric to add

- see effects of various adjustment levels
- make a 10% solution (10g Tartaric acid in 100 ml water).
- This is equivalent to 1g/L of acid
- set up several glasses —100ml of juice/wine and a control
- add 1, 2, 3 ml of the solution, taste and measure pH in each
- quick and accurate

Direct additions: simple, gradual, don't dilute, mix thoroughly, wait, measure change, taste, repeat until objective is reached.

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