Winemaking and Tartrate Instability

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Tartrate Instability

- The solubility of tartaric acid in wine varies dramatically with changes in **temperature** and **%alcohol**.
- Solubility decreases as temperature falls.
- Solubility decreases as %alcohol increases.
- As a result of the increase in %alcohol following fermentation, many wines become supersaturated with tartaric acid. This condition leads to “tartrate instability”.

Tartrate Instability

- Supersaturated tartaric acid will eventually "fall out" of solution.
- Formation of unsightly (but harmless) sediment of yellowish or reddish crystals composed primarily of potassium bitartrate (KHT) (a product of tartaric acid chemistry)

How can the winemaker avoid the precipitation of bitartrate sediment in their bottled wine?

Cold Stabilization

- Some of the excess bitartrates can be "coerced" out of the wine (prior to bottling) by reducing the temperature of the wine to just above the freezing point (e.g., 25° F) and holding it there for about 2 weeks.

- Chilling the wine significantly reduces the solubility of the bitartrates and forces them to precipitate in the tank/carboy (rather than in the bottle). Followed by racking/filtering.

Effects of Cold Stabilization on pH

- If the wine **pH ≥ 3.9**
  Cold stabilization causes an increase in pH.

- If the wine **pH < 3.9**
  Cold stabilization causes a decrease in pH.
  (Lower pH associated with greater pH drop)

- **How can this be?**

Effects of Cold Stabilization on pH

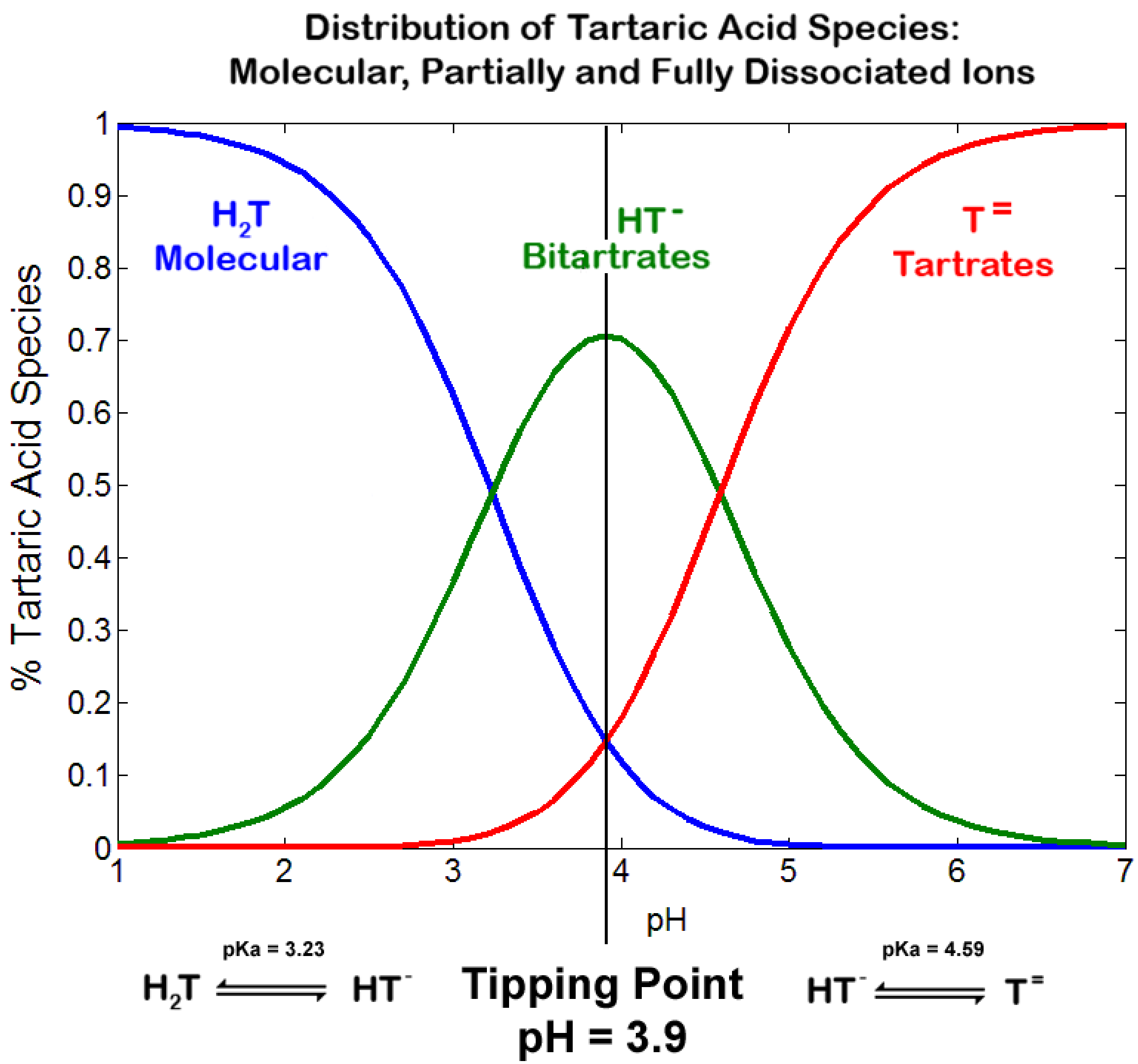
- To explain the bidirectional influence on pH we'll need to do a bit of "heavy lifting"

- We'll begin with the equation describing the equilibrium of various "species" of tartaric acid:

$$H_2T \underset{}{\overset{pKa=3.23}{\rightleftharpoons}} HT^- \overset{pKa=4.59}{\rightleftharpoons} T^=$$

Molecular — Bitartrate ion — Tartrate ion

Now let's see a graphical display of this relationship…



- Cold causes Bitartrates to precipitate out
- Chemical reactions work to maintain equilibrium

When **pH < 3.9** the dominant equilibrium reaction converts H_2T to HT^- Each such conversion adds a free H^+ ion to wine (Decreasing pH)

When **pH > 3.9** the dominant equilibrium reaction converts $T^=$ to HT^-. Each such conversion consumes a free H^+ ion (Increasing the pH)

Summary

Effects of Cold Stabilization upon Wine pH

When wine $pH < 3.9$

Any loss of bitartrates due to cold stabilization results in an imbalance in the equilibrium between the molecular form of tartaric acid (H_2T) and the bitartrate form (HT^-). Equilibrium is quickly restored by the conversion of H_2T to HT^-. This conversion processes frees-up H^+ ions and consequently decreases the pH of the wine.

When wine $pH \geq 3.9$

Any loss of bitartrates due to cold stabilization results in an imbalance in the equilibrium between the doubly-ionized form of tartaric acid ($T^{=}$) and the bitartrate form (HT^-). Equilibrium is restored by the conversion of $T^{=}$ to HT^-. This conversion processes uses-up free H^+ ions and consequently increases the pH of the wine.

Revision Notes

The previous version of this presentation reported that the “tipping point” (between pH decreases vs. increases) during cold stabilization occurred at a pH of 3.65. This value is reported by Zocklein, Fugelsang, Gump & Nury (1995; pp. 233-234), Margalit (2004; p. 305) and Pambianchi (2008; p. 145). All of these sources based their estimates on the behavior of tartaric acid species in pure water.

However, Boulton, et al. (1996; pp. 526-534) explains how the behavior of tartaric acid species changes when alcohol and various ionic concentrations are added to an aqueous solution. As a consequence, the actual “tipping point” in table wine appears to be somewhere in the vicinity of pH = 3.9. Butzke (2010; pp. 354-355) concurs with this revised estimate.

References

Boulton, RB, Singleton, VL, Bisson, LF & Kunkee, RE (1996). Principles and practices of winemaking. New York: Chapman & Hall.

Butzke, CE (Ed.)(2010). Winemaking problems solved. Boca Raton, FL: CRC Press.

Margalit, Y. (2004). Concepts in wine chemistry (2nd edition). San Francisco: Wine Appreciation Guild.

Pambianchi, D. (2008). Techniques in home winemaking. Montreal, PQ: Véhicule Press.

Zoecklein, BW, Fugelsang, KC, Gump, BH & Nury, FS (1995). Wine analysis and production. New York: Chapman & Hall.