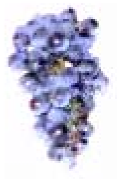

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Coordination Draft
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pH

by

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***pH**, a scale of measurement of the concentration of the effective, active ACIDITY in a solution and an important statistic, of relevance to how vines grow, how grapes ripen, and how wine tastes, looks, and lasts.* [i]

pH—a most important variable

pH is (perhaps) the most important variable for winegrowers and winemakers. pH plays an important role in the vineyard, in the winery, and in the barrel. Although the consumer may be largely unaware of pH, it is a variable that is monitored closely by those involved in growing the grapes and the making the wine.

Soil pH is an indicator of potential nutrient uptake by the grapevine. Grape pH is an indicator of physiological ripeness of the grape. Juice and wine pH is an indicator of the microbiological stability of the wine and various behavioral characteristics and interactions experienced during winemaking and aging.

In this paper, pH and its role in vines and wines will be explored.[ii]

pH—just what is it?[iii]

pH is the concentration of hydrogen ions in acqueous solutions and is responsible for all acid properties. Mathematically, pH is expressed as the negative logrithm of H^+, the hydrogen ion:

$$\mathrm{pH} = \log\,[1/H^+] = -\log\,[H^+]$$

Water ionizes slightly to form:

$$H_2O = H^+ + OH^-$$

Water, at 25°C (77°F), is:

$$0.00001\% = 0.0000001 = 1 \times 10^{-7} \text{ ionized.}$$

There is an equal concentration of H^+ cations and OH^- anions. Each has a concentration of 1×10^{-7}; pure water is considered neutral with pH = 7.0:

$$\mathrm{pH} = -\log\,[H^+] = -\log 10^{-7} = 7$$

$$\mathrm{pOH} = -\log\,[OH^-] = -\log 10^{-7} = 7$$

$$\mathrm{pH} + \mathrm{pOH} = -\log K_W = 14.00$$

where w is pure water. pH ranges from 0 to 14.

Solutions with a pH less than 7.0 are considered acidic and those with a pH greater than 7.0 are considered basic (or alkaline). Wine pH generally varies by a factor of 10—from 3.0 to 4.0.

It is important to note that the pH of a solution measures the concentration of <u>dissociated</u> protons—H^+ being the acidic proton in question—and not the total concentration of acid in a solution.

pH and the vine

Soil pH and Nutrition—Of over 100 chemical elements known today, only 16 are essential to plants. Three elements—carbon (C), hydrogen (H), and oxygen (O)—are derived primarily from air and water and become—via photosynthesis in the leaf—the sugars that, in turn, become ethanol and CO_2 during the winemaking process.

Photosynthesis

$$\underset{\text{carbon dioxide}}{6\,CO_2} + \underset{\text{water}}{6\,H_2O} \xrightarrow{\text{light}} \underset{\text{sugars}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6\,O_2}$$

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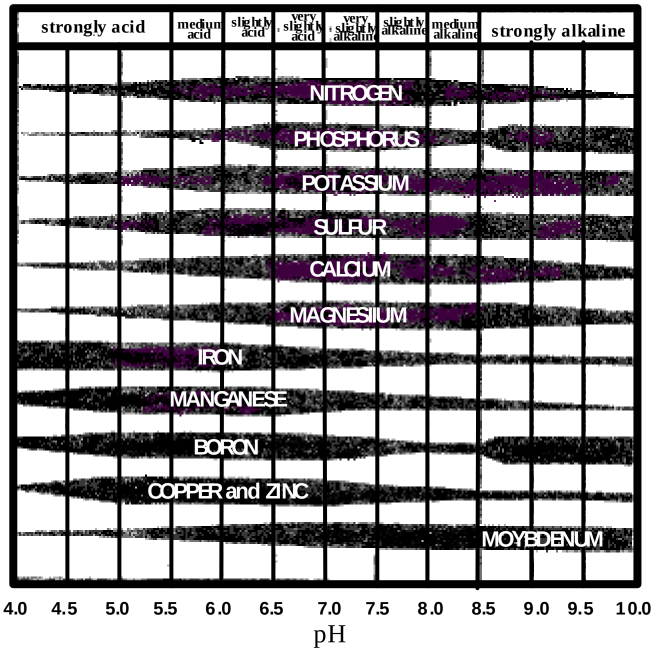
The other 13 elements, normally absorbed from soil by the vine roots, are subdivided into three categories:[iv]

- Primary nutrients: Nitrogen (N), phosphorus (P), and potassium (K)
- Secondary nutrients: Sulfur (S), calcium (Ca), and magnesium (Mg)
- Micronutrients: Zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), boron (B), molybdenum (Mo), and chlorine (Cl)

The potential availability of these 13 essential plant nutrients is a function of pH:



An ideal soil pH is 6.5 or so. Most winegrowers submit a soil or petiole sample for laboratory analysis and apply fertilizers to maintain the correct soil and plant nutrient levels.

Grape pH and Potassium[v]—Excess potassium in the soil can result in wines too high in pH (although also high in titratable acidity). This problem arises when grapevines are planted for the first time but declines somewhat as harvested crops remove potassium from the soil.

Grape pH and Climate—In general, cool regions produce wines with low pH and hot regions produce wines with high pH [OCW].

Grape pH and Harvest—As harvest approaches, focus is mostly on grape attributes such as taste and look, °Brix (°B), titratable acidity (TA), and pH. °B—roughly the percent of sugar in the grape—serves as the primary *analytical* metric. As the berries ripen, °B increases from 5 or so to the low-to-mid 20s, TA decreases from 20 g/L or so to 6-10 g/L, and pH increases to the 3-to-4 range (but too slowly to serve as a practical measure). *Botrytis cinera* (grape mold) can reduce TA and increase pH.[vi]

pH and TA—Grapes, must, juice, and wine contain acids [WAP, p 76; PPW pp 521-523]:

Total Acidity = Fixed Acidity + Volatile Acidity

Fixed acids include tartaric (the most prominent at 5-10 g/L), malic (at 2-4 g/L), plus smaller quantities of amino acids (arginine, proline), lactic, succinic, and inorganic acids.

Volatile acids include acetic acid, propionic, butyric, and sulfurous acids.

Equilibrium for, say, one of the fixed acids is:

$$\mathrm{HA(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}\ \mathrm{(aq)}$$

Or, taking away the water and the aqueous notation, the HA molecule (left) is in equilibrium with the ionized H^+ and A^- (right):

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

Here the TA is the H in the HA plus the H^+. pH is represented by only the H^+ ion. The pH at which the molecule (left) and ions (right) are in equilibrium—this is the pK_a or dissociation constant—varies for each acid. At equilibrium, 50% of the hydrogen is dissociated as H^+ ions (and the law of mass action states that equilibrium is maintained in solutions).

Strictly speaking, TA is expressed in terms of tartaric acid (U.S.) or sulfuric acid (France) and is measured by titrating the juice or wine with a strong base (*e.g.*, NaOH) to a pH of 8.2 (U.S.) or a pH of 7.0 (France).

If the pH of a must or juice is too high, say above 3.7, it can be reduced by adding tartaric acid that, seeking equilibrium, dissociates H+ protons thereby lowering pH. Because total hydrogen (on the left plus the right) increases, TA increases.

pH is important in winemaking because it affects microbial stability and spoilage.

TA has no effect on microbial activity but is very important to the sensory qualities of the finished wine (PPW, p. 521-523).

pH and the wine

pH influences and is influenced by various acids and other constituents of juice and wine as well as by other factors of the winemaking process.

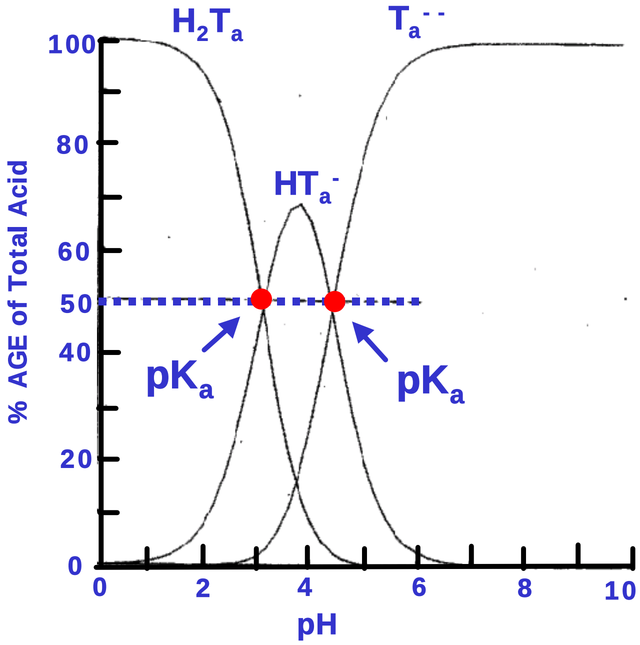
pH and titratable acidity (TA) targets depend on the variety and the winemaker's style.

Typical pH & TA Targets		
Variety	**pH**	**TA**
Sauvignon blanc	3.2	7.0 g/L
Chardonnay	3.4	6.5 g/L
Pinot noir	3.7	6.0 g/L
Cabernet Sauvignon	3.85	5.0 g/L

Dissociation (or Ionization) Constants—The concentration of dissociated H+ ions for various acids in must, juice, and wine is a function of pH.

Many acids, such as tartaric—$C_4H_6O_6$ or, to split the H_2 and T_a parts: $H_2C_4H_4O_6$)—have more than one form and more than one equilibrium state:

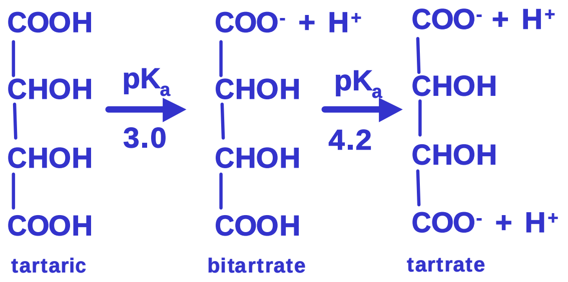
- Molecular tartaric acid H_2T_a
- Bitartrate ion HT_a^-
- Tartrate ion T_a^{--}



For tartaric acid there are two pK$_a$—50% crossover points—one at a pH of 3.0 and another at a pH of 4.2. Also note that the bitartrate (HT_a^-) peaks at a pH of about 3.6. The equilibrium relationships are represented by:

$$\underset{\text{tartaric}}{H_2T_a} \xrightleftharpoons{3.0} H^+ + \underset{\text{bitartrate}}{HT_a^-} \xrightleftharpoons{4.2} 2\,H^+ + \underset{\text{tartrate}}{T_a^{--}}$$

Bitartrate Stability—The tartaric relationships can also be shown as:



The major physical instability in bottled wines is the precipitation of potassium bitartrate and calcium bitartrate. Stability should be achieved in the cellar not in the bottle. Between pHs of 3.0 and 4.0, the bitartrate fraction increases from 43% to 71% with a peak of 73% at 3.8. At the same time, the fraction in tartrate form rises from 1% to 19%, roughly doubling over the 3.7 - 4.0 range [PPW, pp 320-321].

Tartaric acid has two titratable protons. When you cold stabilize Sauvignon blanc at pH of 3.2 or a Chardonnay at pH of 3.4, potassium bitartrate (KHT_a) precipitates out of solution [WAP, p. 233-234]. Here, the bitartrate fraction predominates:

$$K^+ + HT_a^- = KHT_a$$

This <u>reduces</u> pH—by as much as 0.2—as one free H^+ proton is released per molecule of KHT_a precipitated (equilibrium moves to the right as HT_a dissociates to replace the T_a^- and adds an H^+ in the process). TA decreases by as much as 2g/L (as some H is precipitated out of solution).

At pH values above 3.65, KHT_a, where the tartrate fraction comes into prominence (10 times more at pH 4 than 3), precipitation <u>raises</u> pH as one H^+ proton combines with one tartrate ion (and equilbrium moves to the left with fewer protons):

$$H^+ + T_a^{--} = HT_a^-$$

TA also decreases for the higher pH wines as some hydrogen still binds and falls out solution.

Winemaking Practices—Seed breakage causes an elevation of 0.2 to 0.3 in pH [WAP, p 61].

Malolatic fermentation increases pH.

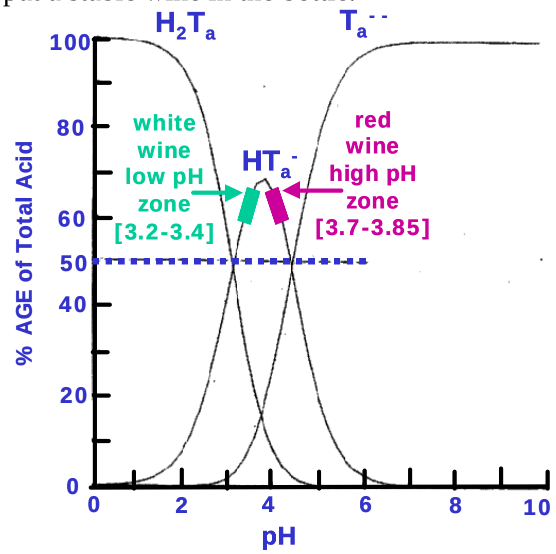
"It is well known that high pH wines (highly ripe grapes from warm vineyards) do not age well, are poor in quality, and deteriorate badly. … pH has such a great effect on wine oxidation …." [PPW p 410] Yet many extraordinary wines are high pH.

high pH winemaking[vii]

A wine's first duty is to be red.

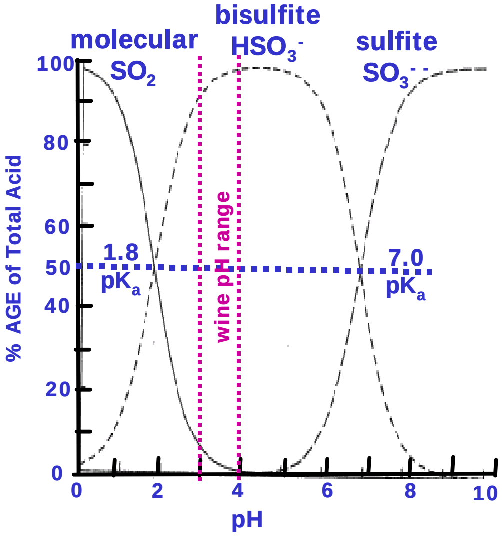
anon.

Low pH and high pH winemaking require different approaches. In high pH winemaking, spoilage and other negatives are more likely to occur. The approach by Vinovation's Clark Smith—an advocate of big, hairy, high pH reds—is to deal with microbial activity at the winery and put a stable wine in the bottle.



As noted on the previous page, in high pH wines, tartrate precipitation tends to raise pH (of an already high pH wine) and lower TA.

At high pH, the opportunity for oxidation and spoilage is much greater than at low pH. Hence, free sulfur dioxide (SO_2)—essentially bisulfite (SO_2^{--})—comes into play as a spoilage inhibitor and, at the same time (<u>over</u> <u>time</u>), lowers pH and raises TA thus counteracting the tartrate influence.



This reversal occurs over an extended time period in the barrel as the sulfite oxidizes into sulfate (this causing a bisulfite to release a proton):

$$\underset{\text{molecular}}{H_2O + SO_2} \overset{1.8}{\rightleftharpoons} H^+ + \underset{\text{bisulfite}}{HSO_3^-} \overset{7.0}{\rightleftharpoons} 2\,H^+ + \underset{\text{sulfite}}{SO_3^{--}} \;[\,+\,1/2\,O_2 = \underset{\text{sulfate}}{SO_4^{--}}\,]$$

In high pH winemaking, Smith suggests: (1) Take care that in blending two stable lots of wine that the combination does not supply spoilage elements; (2) Free SO_2 must be maintained to inhibit oxidation and control spoilage. Oxygen reacts with phenolics leading to their polymerization that can yield hydrogen peroxide that is reduced by the bisulfite; (3) Sanitation is essential to reduce spoilage and topping is essential to reduce oxidation (although topping introduces oxygen); (4) Complete fermentation at elevated temperatures is desirable; (5) The wine should undergo all potential microbial activity at the winery; (6) Micro-oxygenation can help build structure, round tannins, integrate aromatics and lower reduction; (7) Juice-skin contact introduces 100s of phenols: monomeric phenols contribute to aroma and polymeric phenols (tannins) yield astringency.

conclusions

pH plays a vital role in winemaking relative to spoilage, stability, and titratable acidity.

Although the making of high pH red wines entails risk, the rewards can justify the risks.

Napa Valley Bordeaux blends and Cabernet Sauvignons with price points of $100 or more, are nearly always high pH wines with some at 3.9 or even a bit higher.

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[i] *The Oxford Companion to Wine*, Jancis Robinson, Editor, Oxford University Press (1994) [OCW]

[ii] The material is from three sources: coursework completed at Napa Valley College's Viticulture & Winery Technology Program headed by Dr. Stephen Krebs, classroom material and textbooks, and somewhat modest personal experience in winegrowing and winemaking.

[iii] Fred D. Hess (revised by Arthur L. Thomas), Chemistry Made Simple, Doubleday, New York (1955, 1984)

[iv] Western Fertilizer Handbook, California Fertilizer Association, Interstate Publishers (8th Edition 1995)

[v] Roger Boulton *et al*, *Principles and Practices of Winemaking*, Aspen Publishers (1998), [PPW, p 25]

[vi] Bruce Zoecklein *et al*, *Wine Analysis and Production*, Aspen Publishers (1999), [WAP, p.64]

[vii] Clark Smith, "Winemaking at High pH," http://www.vinovation.com (this paper is currently available from the web site).