UC DAVIS VITICULTURE AND ENOLOGY




UNDERSTANDING WINE ACID CHEMISTRY

OREGON WINE SYMPOSIUM

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Outline

- Background
- Acid species and equilibria in juices and wines
- pH
- Titratable acidity
- Dissociation Curves
- Buffer capacity
- pH adjustments

Background – before V&E

- Grew up in Kansas City, KS
  - Generations of farmers
- BS Chemical Engineering, U of Notre Dame
- Product Development @ Procter & Gamble
  - Pampers diapers
  - Charmin bath tissue

**Interests in agriculture,
chemical reactions, and consumer products**

Background – after V&E

- MS Viticulture & Enology, UC Davis
- PhD Chemical Engineering, UC Davis
  - Heterogeneous catalysis
- Postdoc @ UC Berkeley
- Start-up (fuels industry) in Bay Area

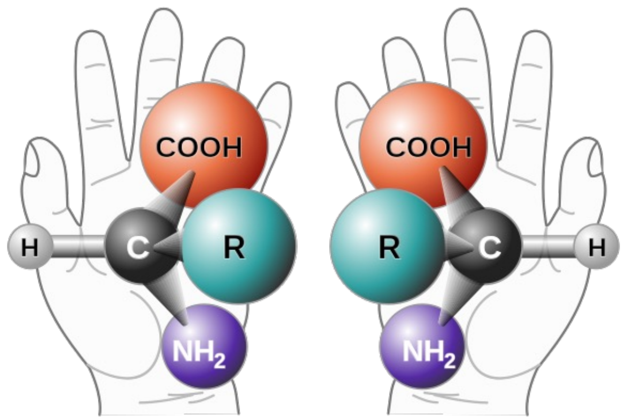
Structure-activity relationships of catalytic and adsorbent materials

The Organic Acids of Juices and Wines

- **Tartaric acid (L-(+); *dextro(+)*): stable backbone of juice and wine acidity, stability associated with solubility of its two salts**
- **Malic acid (L-(+)): second major acid in juice, converted to Lactic in MLF, substrate for other wine spoilage organisms, soluble salts**
- **Lactic acid (L-(+)): in wine after MLF**
- **Traces of Citric acid in Juice, MLF buttery – diacetyl**
- **Succinic formed during fermentation, up to 1 g/L**

Fun Fact: Tartaric acid's role in chiral chemistry

- **In 1832, Jean Baptiste Biot observed its ability to rotate polarized light**
- **In 1847, Louis Pasteur continued this research by investigating the shapes of sodium ammonium tartrate crystals, which he found to be chiral.**



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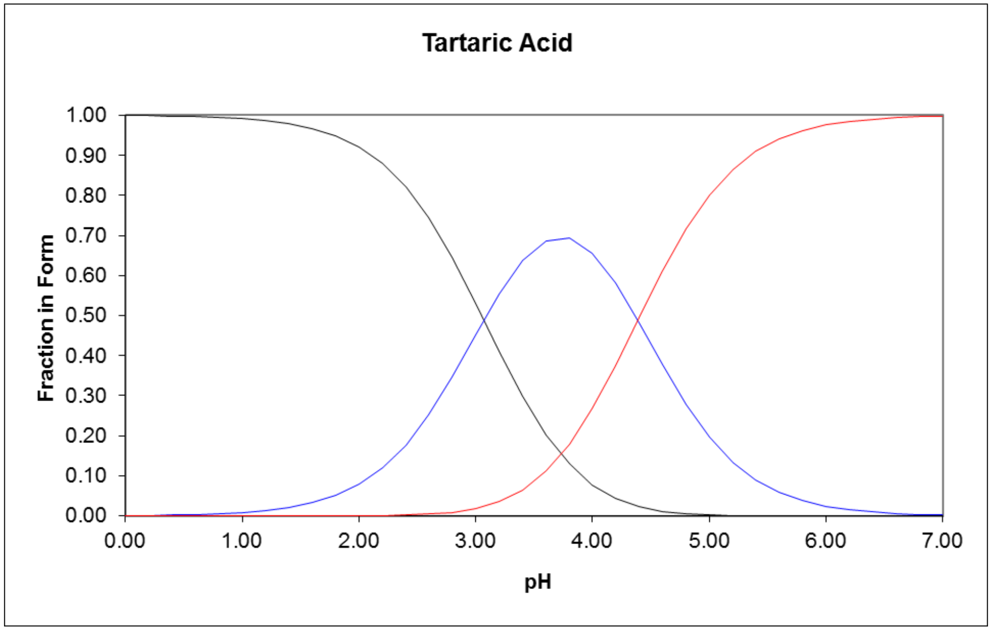
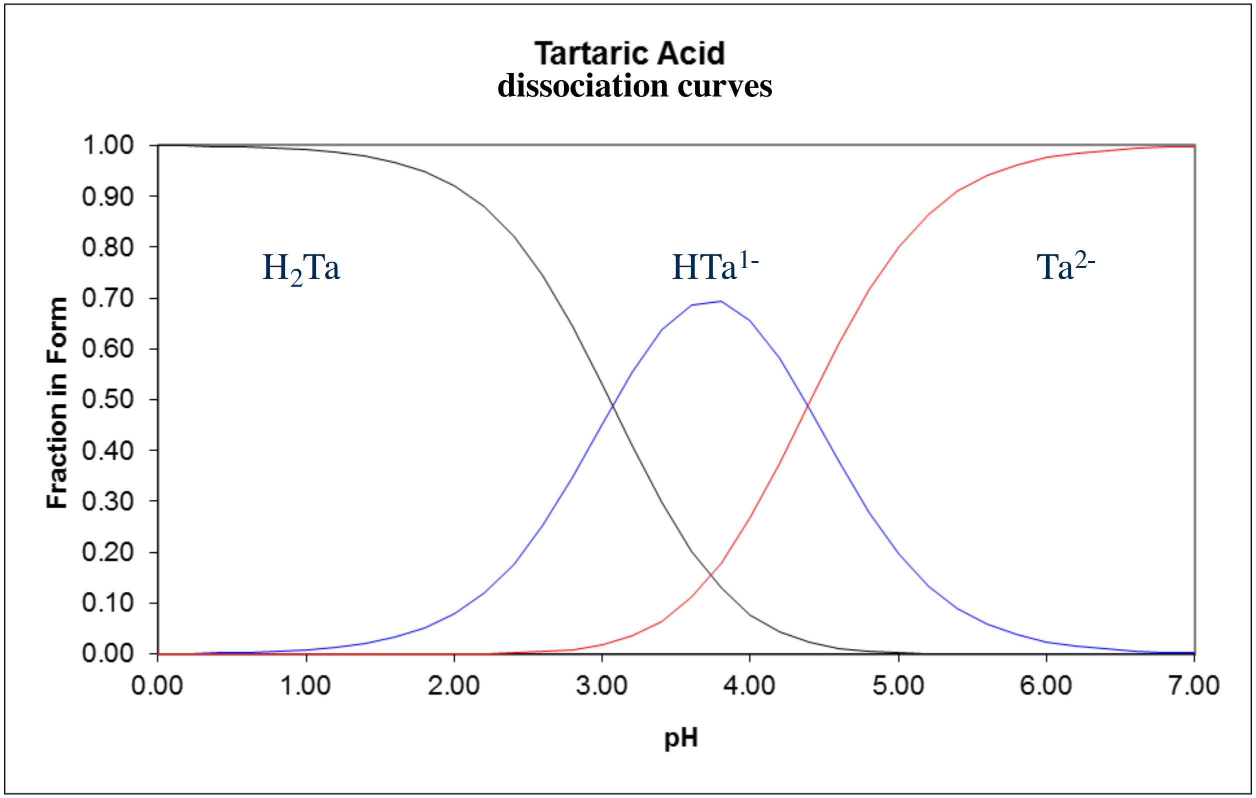
https://en.wikipedia.org/wiki/Tartaric_acid
https://en.wikipedia.org/wiki/Louis_Pasteur
https://en.wikipedia.org/wiki/Jean-Baptiste_Biot
https://en.wikipedia.org/wiki/Chirality_(chemistry)#:~:text=In%20chemistry%2C%20a%20molecule%20or,l%C9%AAti%2F).

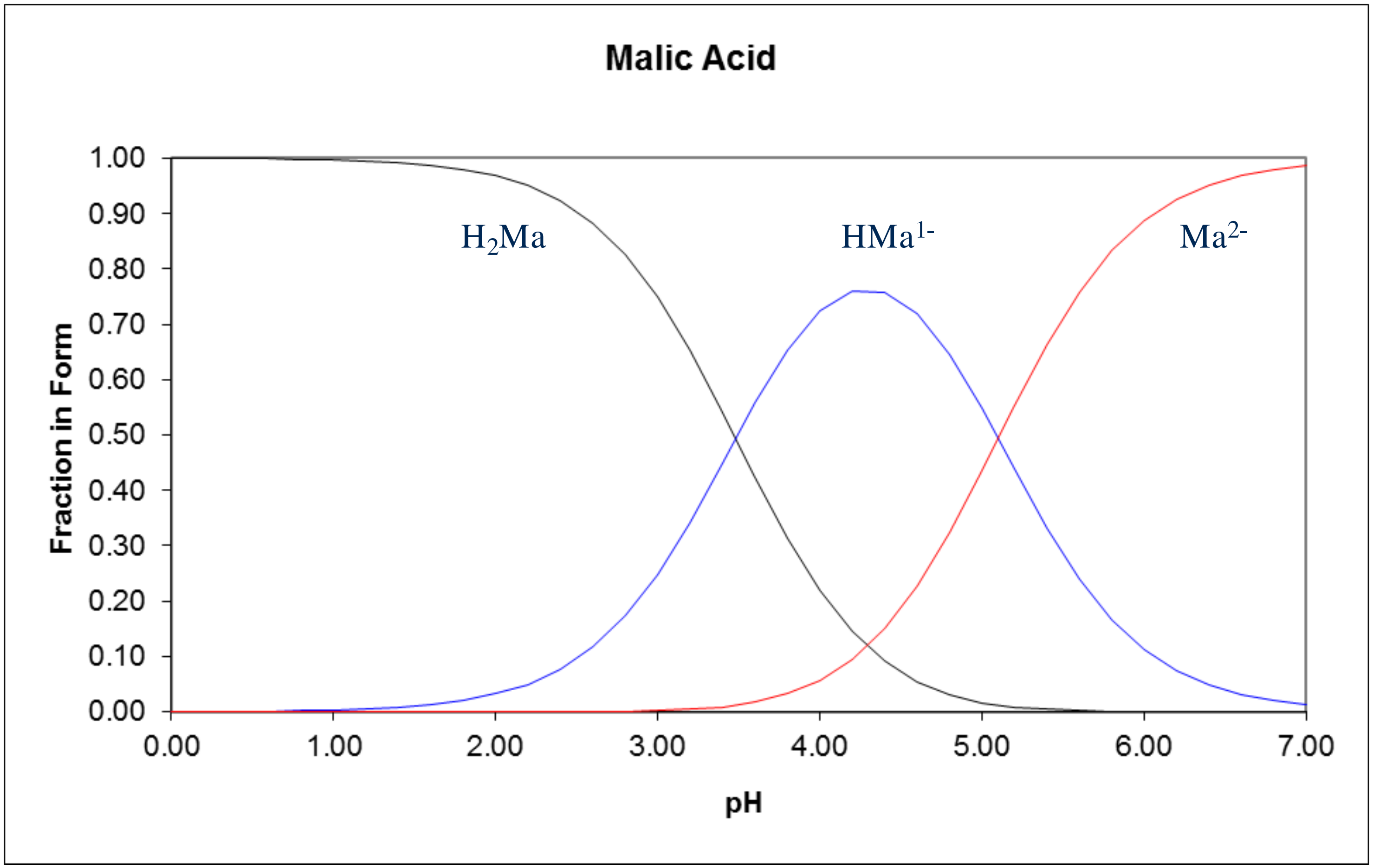
Dissociation Curves

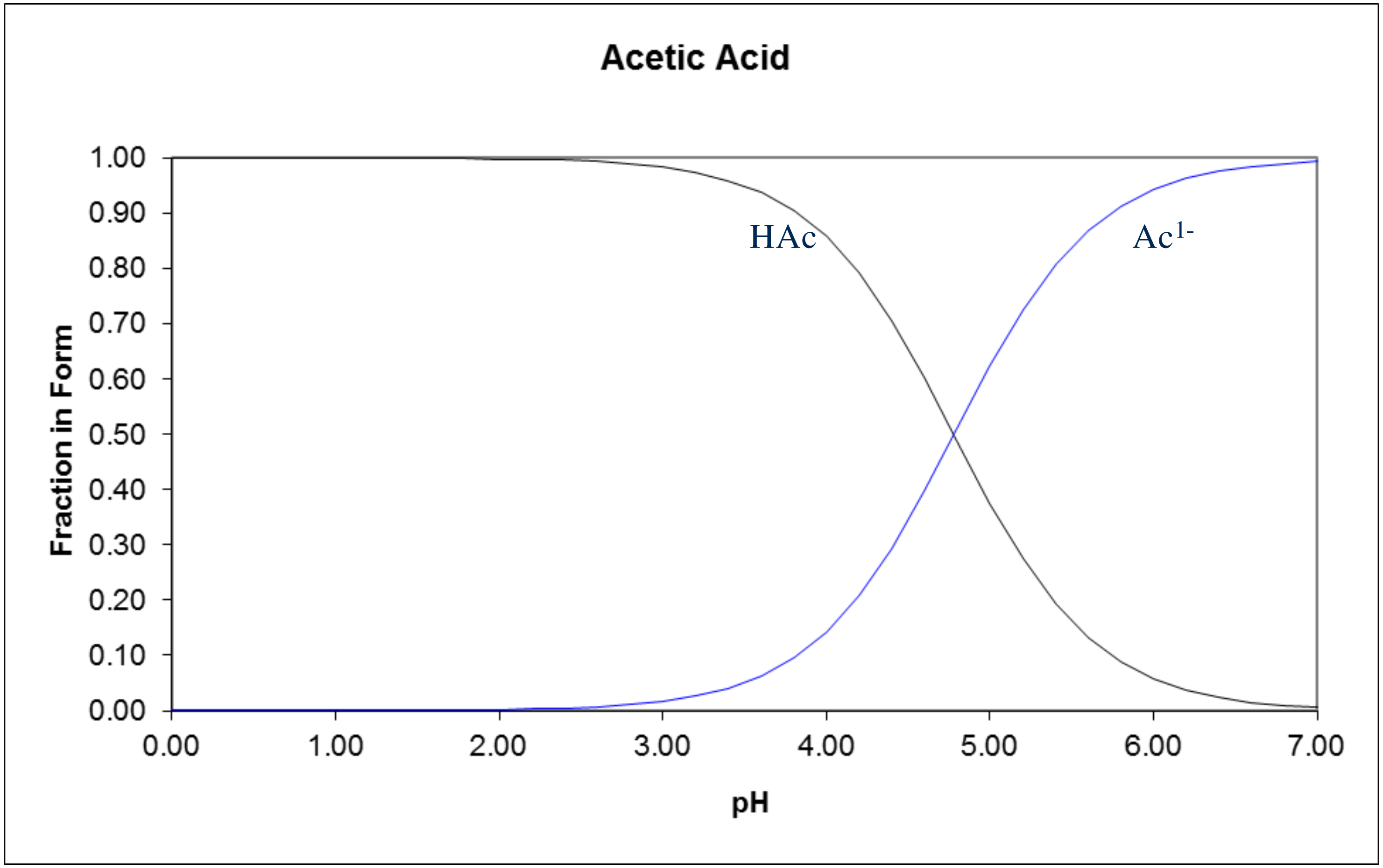
- Mostly diprotic acids with close pKs
- Reactivity, toxicity and volatility are related to different acid entities
- Role of pH can then be understood





$H_2Ta \rightarrow H^+ + HTa^-$ $HTa^- \rightarrow H^+ + Ta^=$


Malic Acid
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Fraction in Form
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
pH
H2Ma
HMa1-
Ma2-

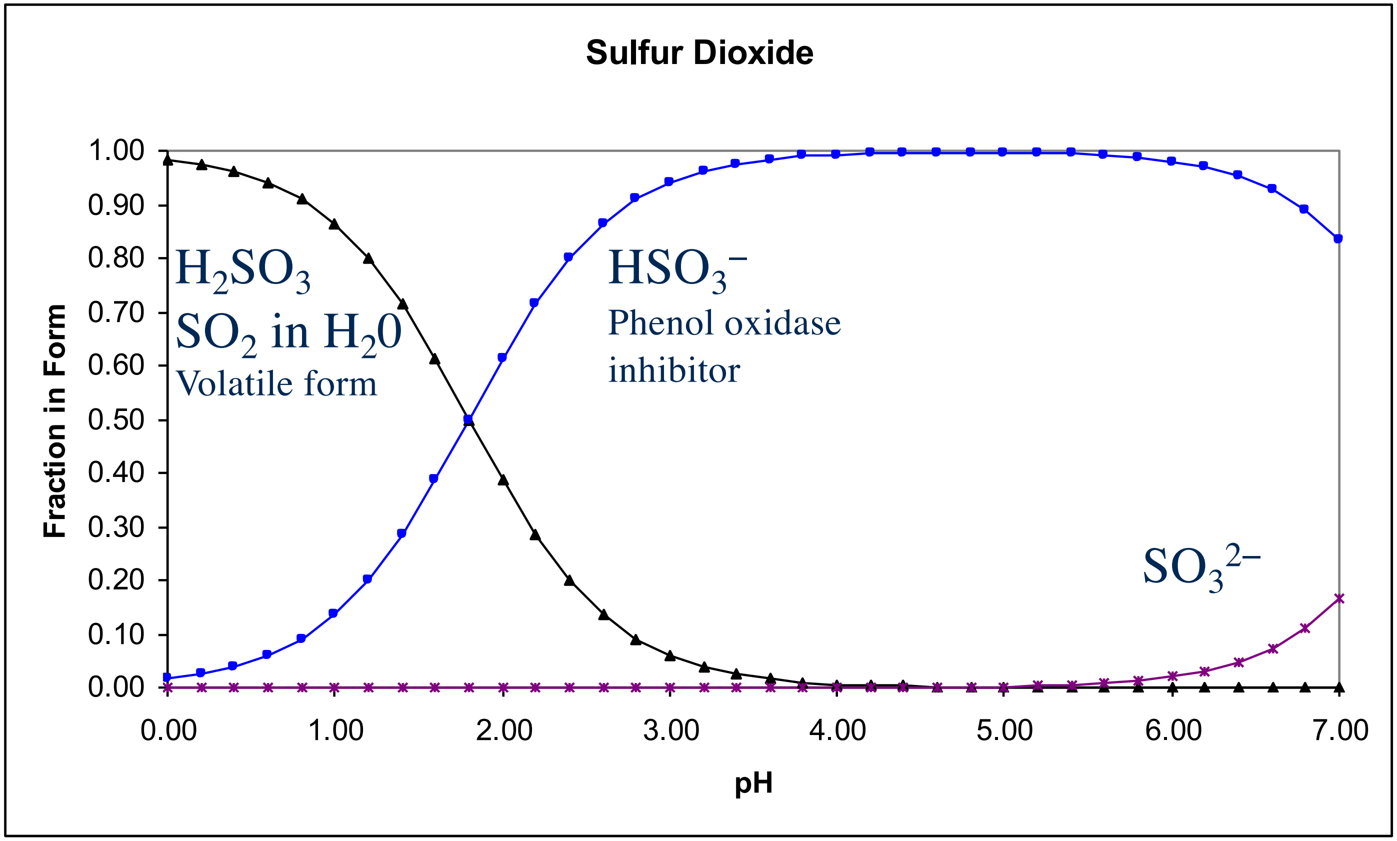


Acetic Acid
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Fraction in Form
HAc
Ac1-
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
pH

pH Values

- Free form of dissociated H^+ ions
- Critical condition during winemaking
- Important for rate and extent of enzyme, physical and chemical reactions
  - Important for acid dissociation, SO_2, acetic, etc.
  - Important for stability of proteins, tartrates
  - Sensory effects on volatility of SO_2
- Recognize impact of pH below 3.6 on wine stability

Sulfur dioxide Dissociation Curves



How the impact of SO_2 depends upon pH

In this example, at pH 3.2, a Free SO_2 level of 21 mg/L is required to attain 0.8 mg/L <u>molecular</u>.

At pH 3.6, more than 50 mg/ are required to achieve the same 0.8 mg/L <u>molecular</u>.

184 *Sulfur Dioxide and Ascorbic Acid*

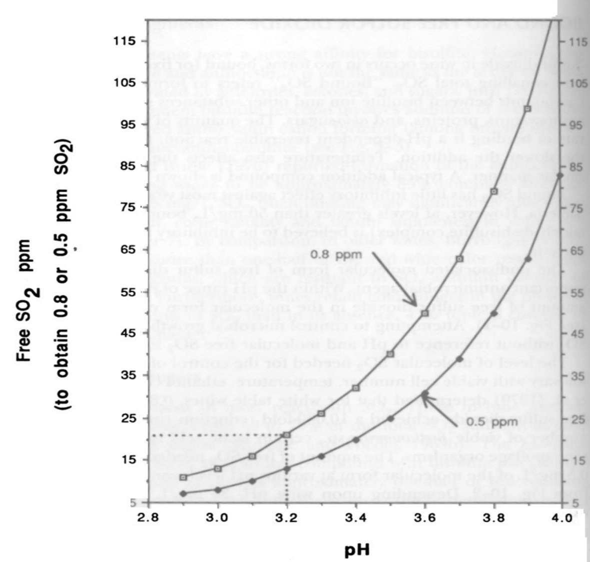
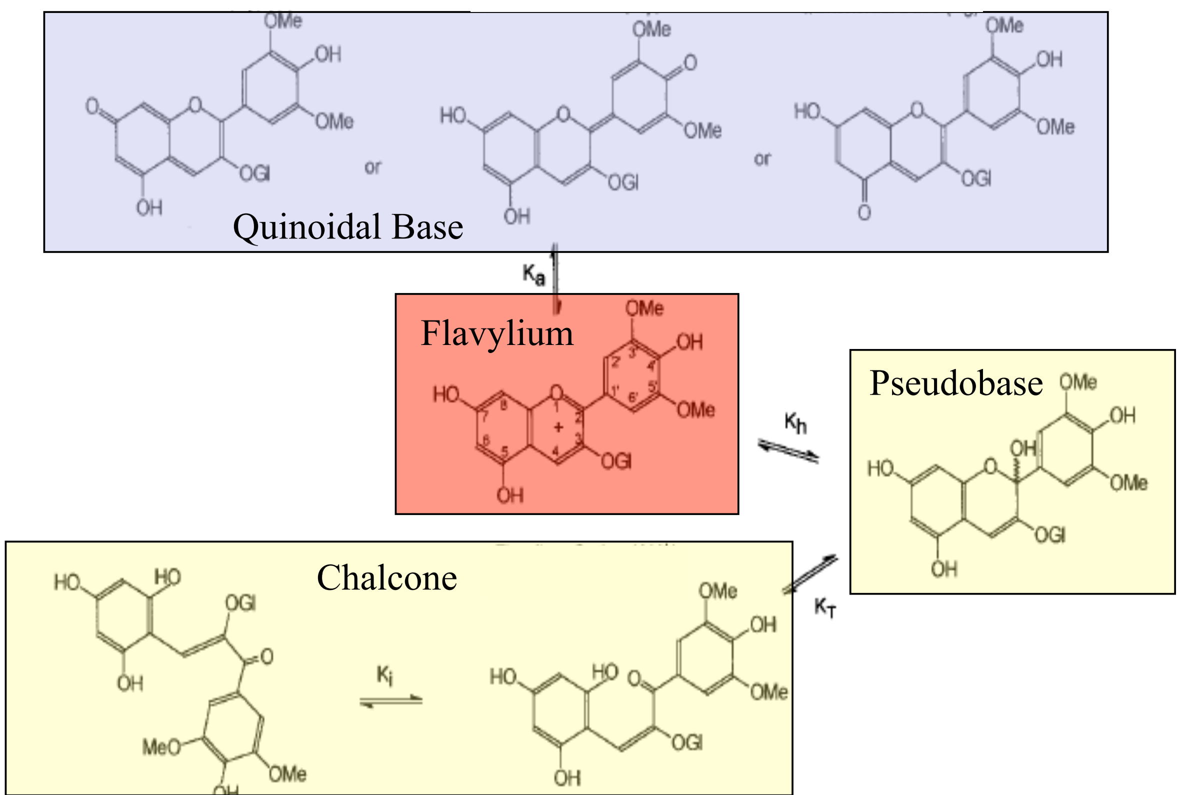


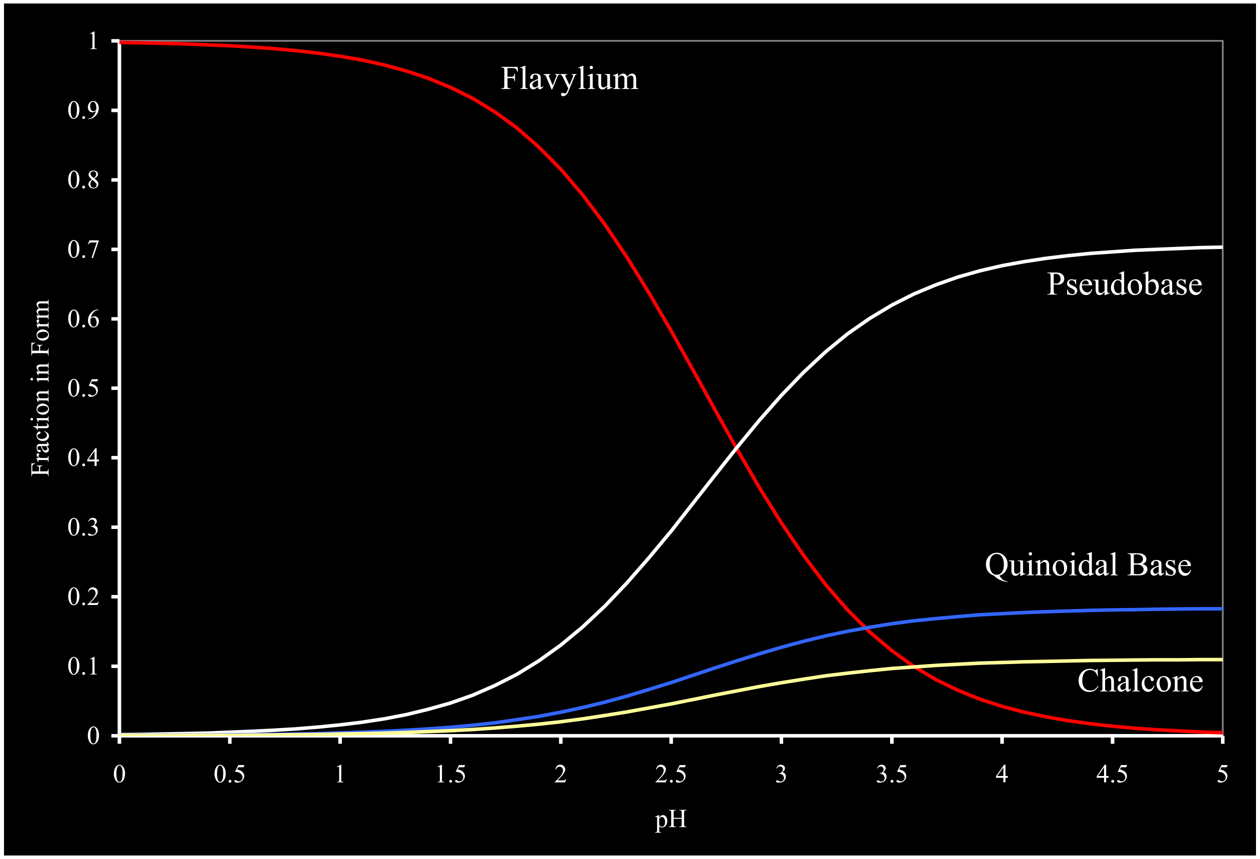
Fig. 10–2. Amounts of free SO_2 needed to obtain 0.5 or 0.8 mg/L (molecular) at various pH levels.

Color of Free Anthocyanins – ionization forms



Houbiers et al. (1998)

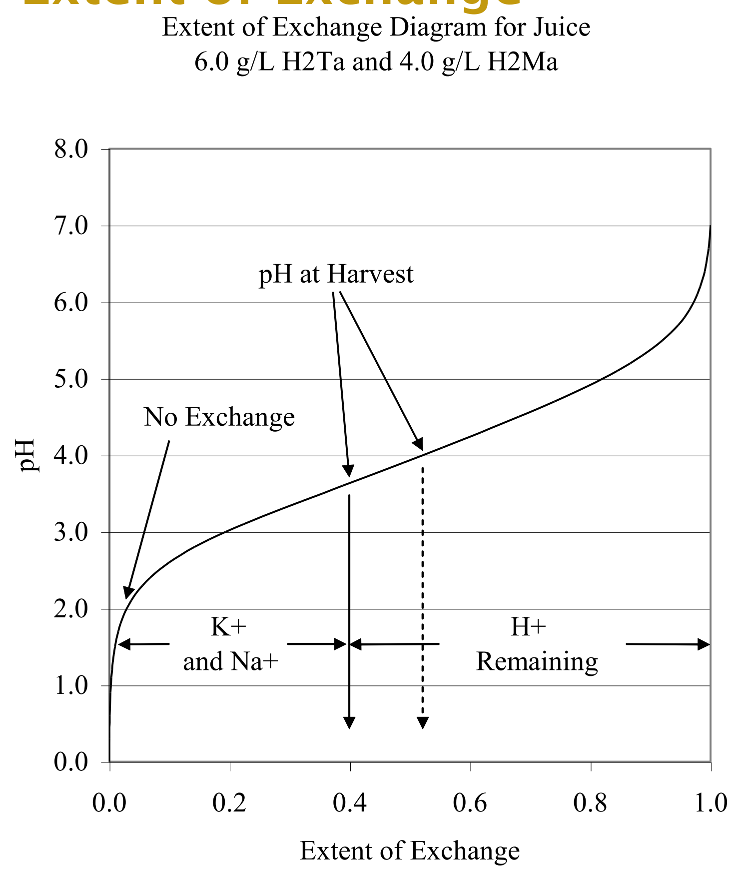
Ionization of Malvidin 3-glucoside



Titratable Acidity

- Recovery of H+ by titration
- Avoid the term “total acidity,” ambiguous
- Less than expected from acid concentrations
- Correlated with sour sensation in the mouth
- Of no significance to rate or extent of enzyme, microbial, physical or chemical reactions during winemaking

Titratable Acidity and Extent of Exchange



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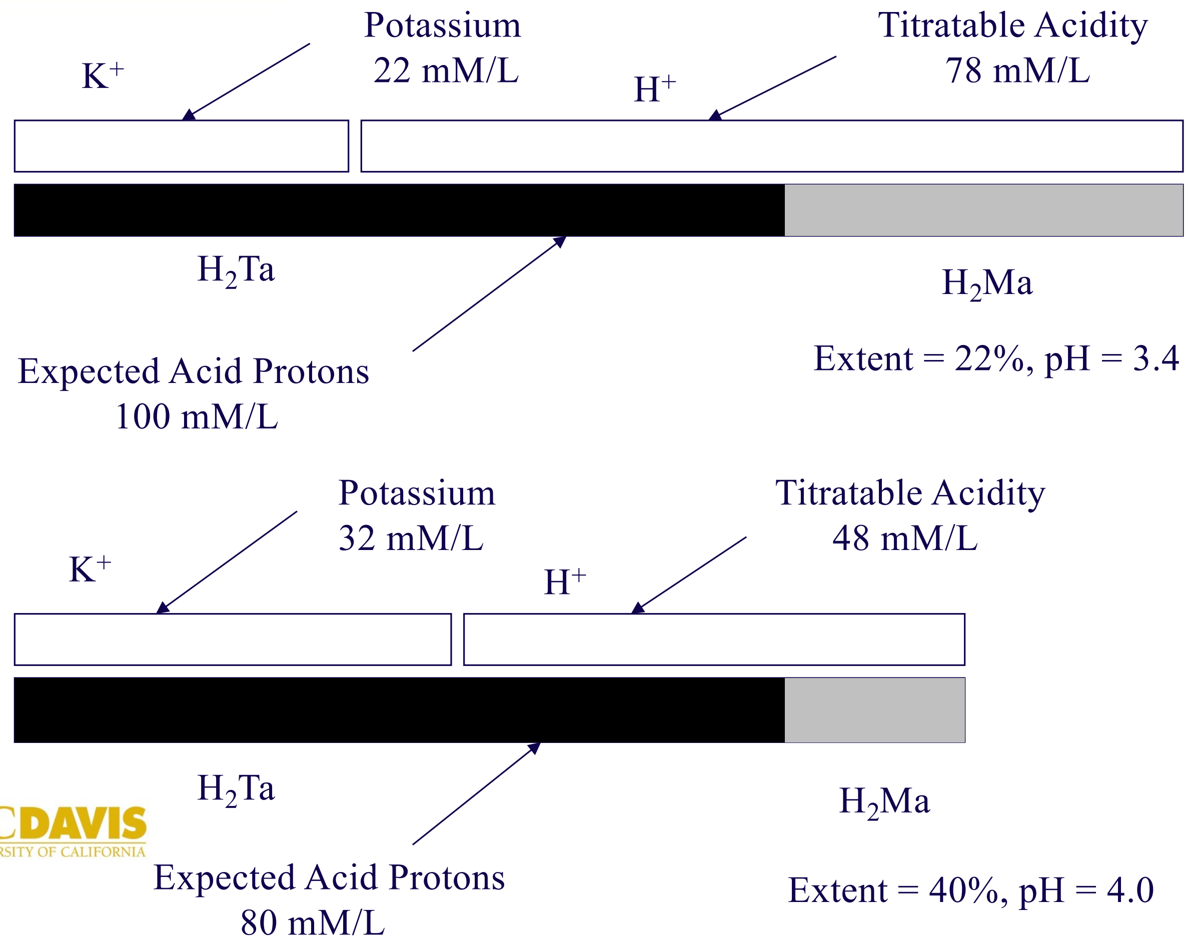
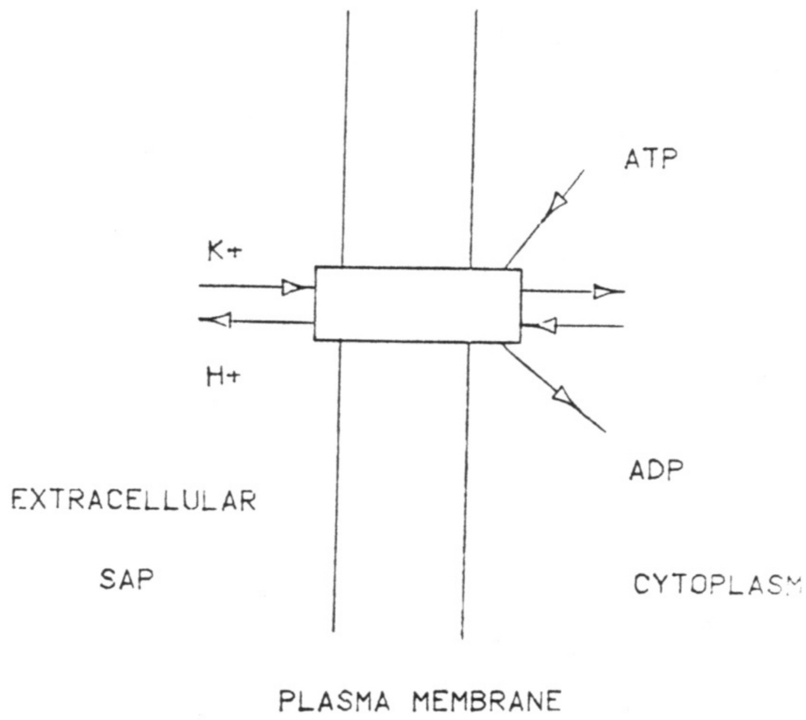

Potassium
22 mM/L
Titratable Acidity
78 mM/L
K+
H+
H2Ta
H2Ma
Expected Acid Protons
100 mM/L
Extent = 22%, pH = 3.4
Potassium
32 mM/L
Titratable Acidity
48 mM/L
K+
H+
H2Ta
H2Ma
Expected Acid Protons
80 mM/L
Extent = 40%, pH = 4.0

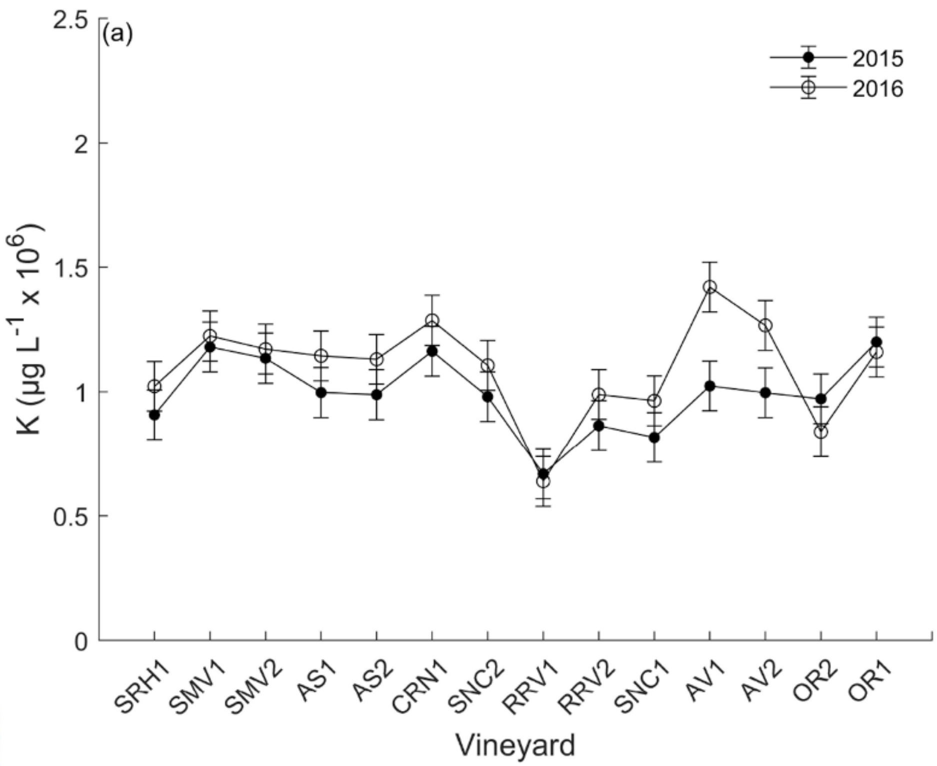
How does exchange of H^+ occur?



Potassium Content and pH

- H+/K+ ATPase in roots, leaves, berries
- Loss of H+ when K+ taken up
- Young vines, lower crop level, high K soils, soil moisture, late harvest can lead to higher pH in grapes (more exchanged)
- Higher crop level, early harvest, older vines, low K soils, dry soils can lead to higher TA and lower pH (less exchanged)

Levels of Potassium in Pinot noir wines



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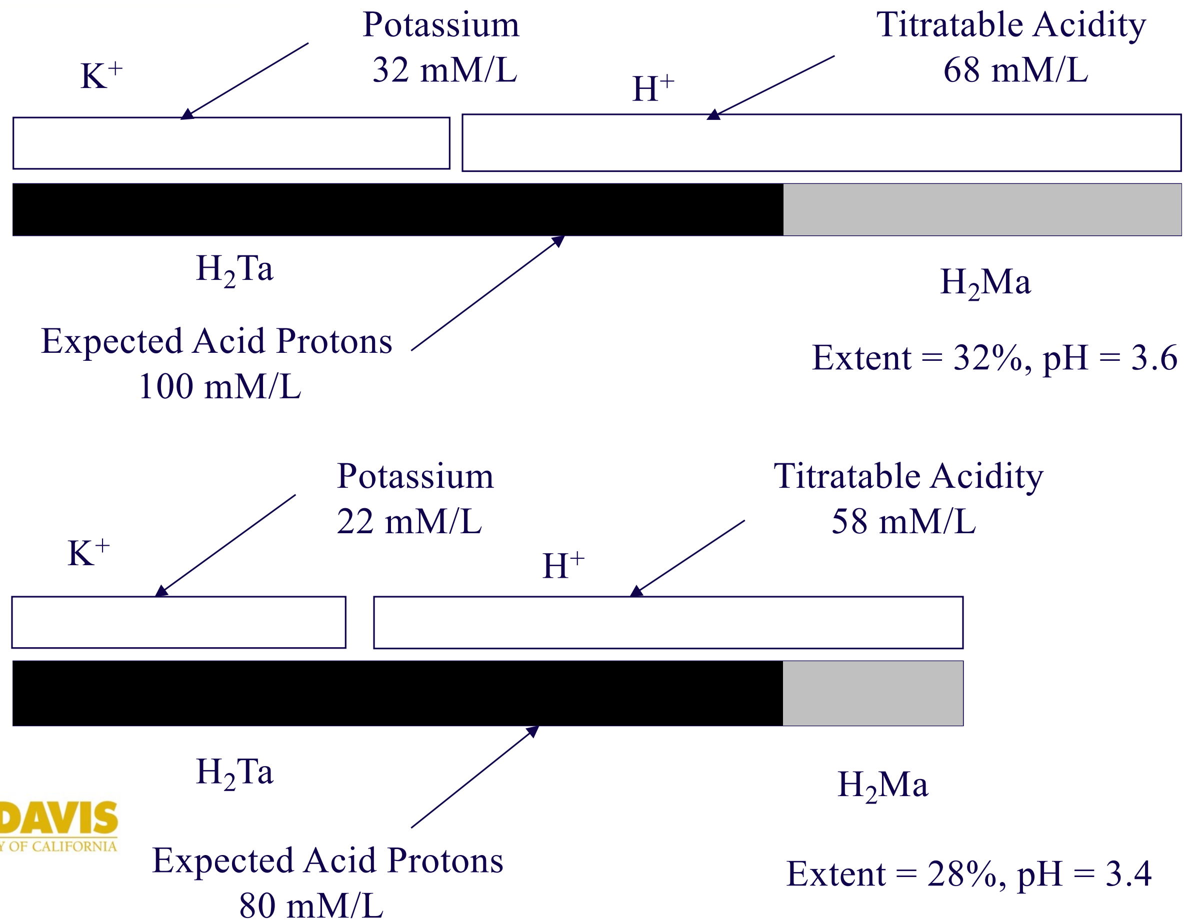
M.M.M. Lima et al., 2021. Food Research International 141 (2021) 110045



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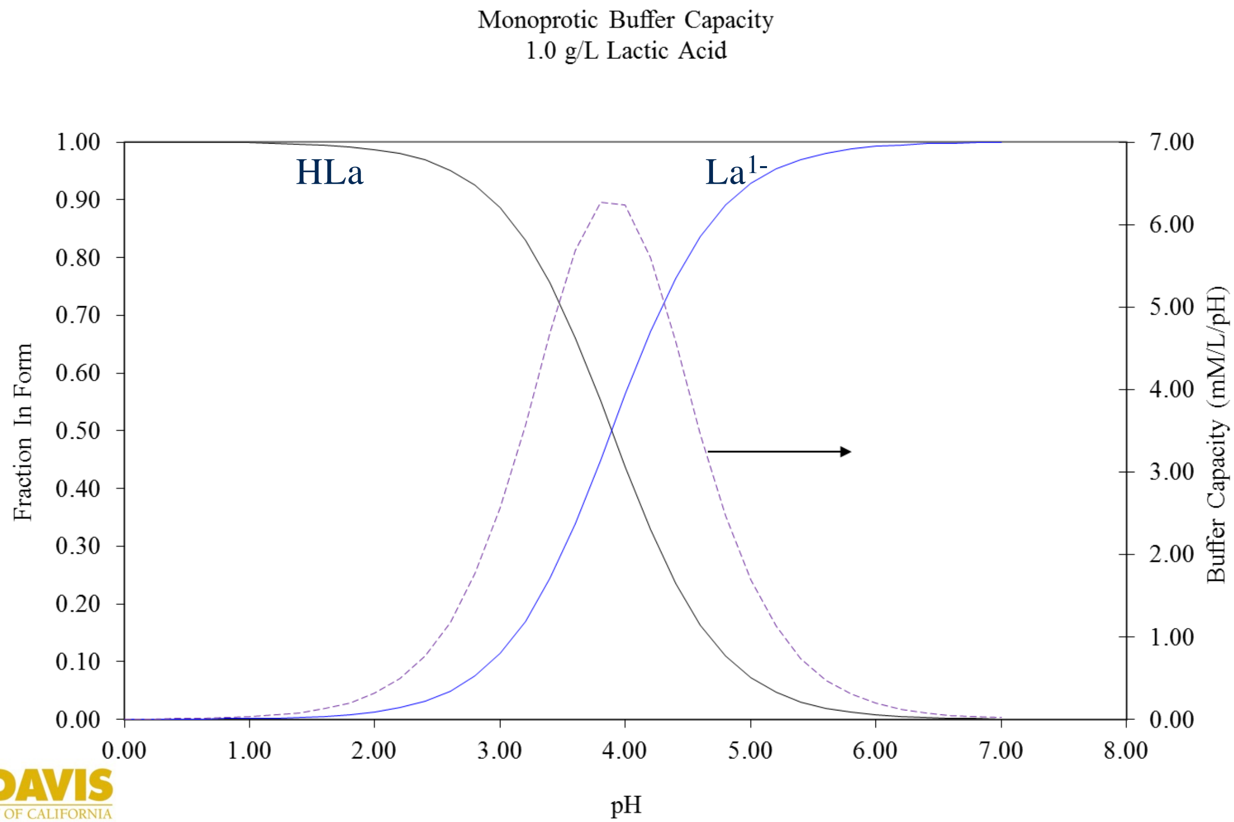
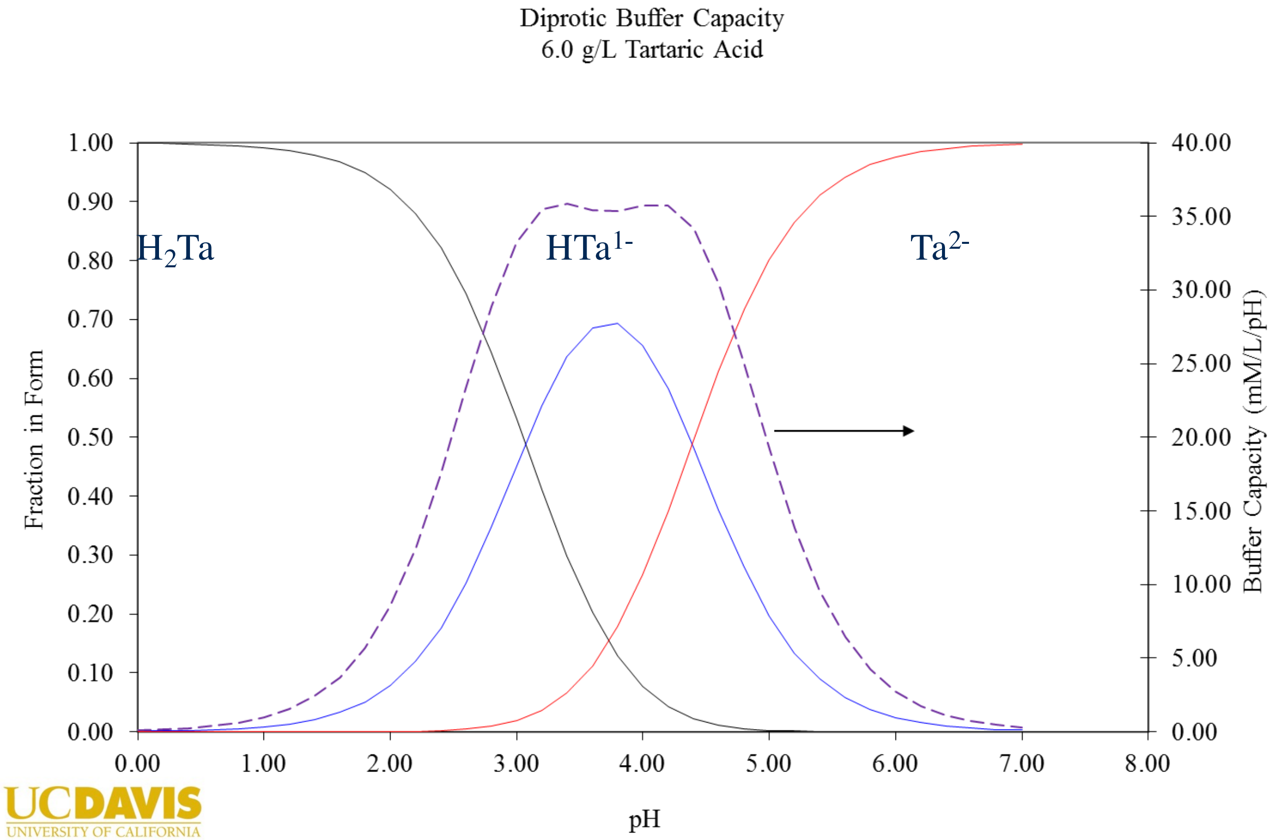
Buffer Capacity and pH Adjustments

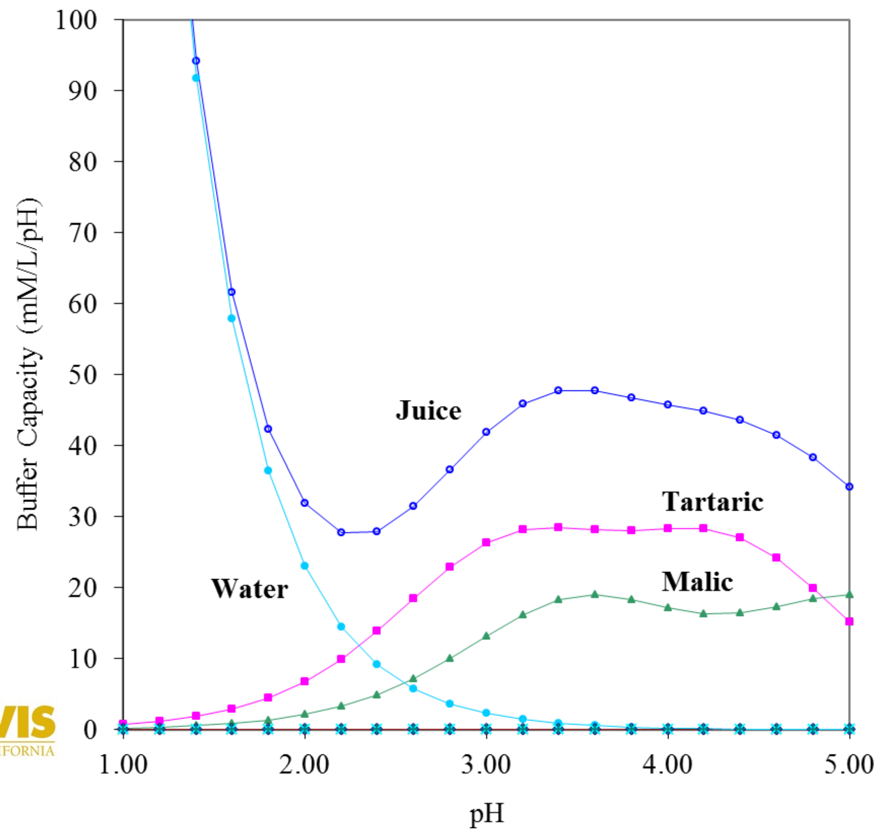
Buffer Capacity

- **"Resistance to change in pH," β (mM/L/pH)**
- **Units are in moles H+ (or OH-) per L required to move the pH by one unit**
- **Proportional to acid concentration**
- **Depends on pH and pKs of the acids**
- **Additive for a mixture of acids**

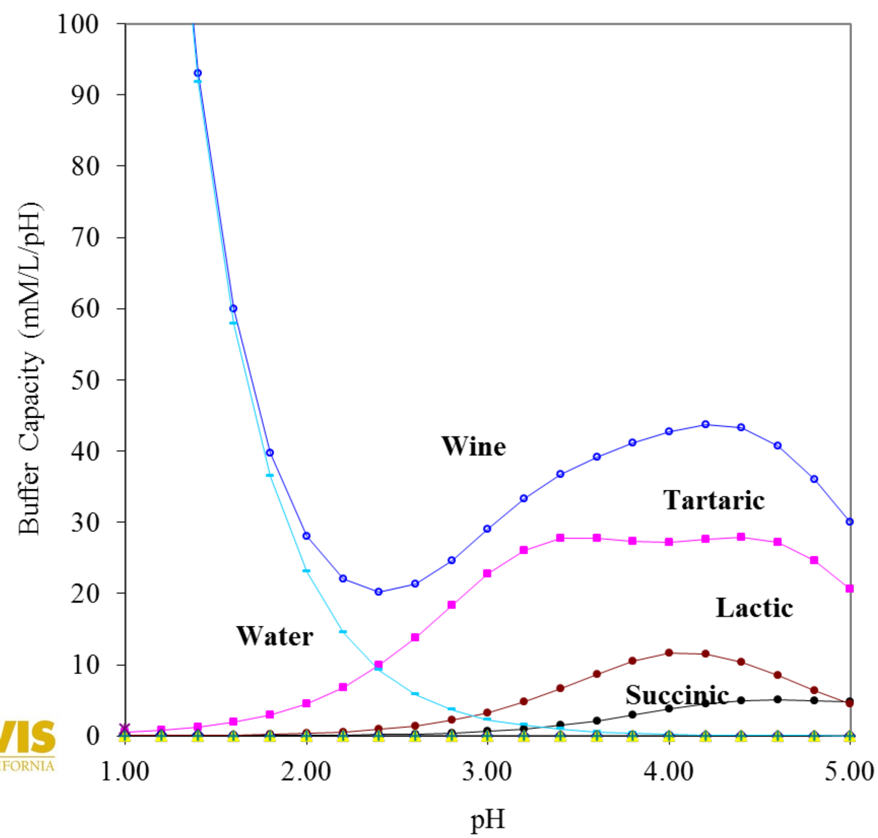

Monoprotic Buffer Capacity
1.0 g/L Lactic Acid
HLa
La1-
Fraction In Form
Buffer Capacity (mM/L/pH)
pH
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00


Diprotic Buffer Capacity
6.0 g/L Tartaric Acid
H_2Ta
HTa^{1-}
Ta^{2-}
Fraction in Form
Buffer Capacity (mM/L/pH)
pH
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00

Buffer Capacity of a Juice



Buffer Capacity of a Wine



pH Adjustments

pH Adjustments

- Lowering of pH
  - Target of ~3.6 or below
- Tartaric acid addition
  - Two effects, dissociation of H+, precipitation of KHTa later, rely on first effect
  - Weak acid, so not all of it will dissociate to H+
  - More effective ionization at higher pH
  - pH change depends on the addition, buffer capacity, and starting pH

Lowering pH

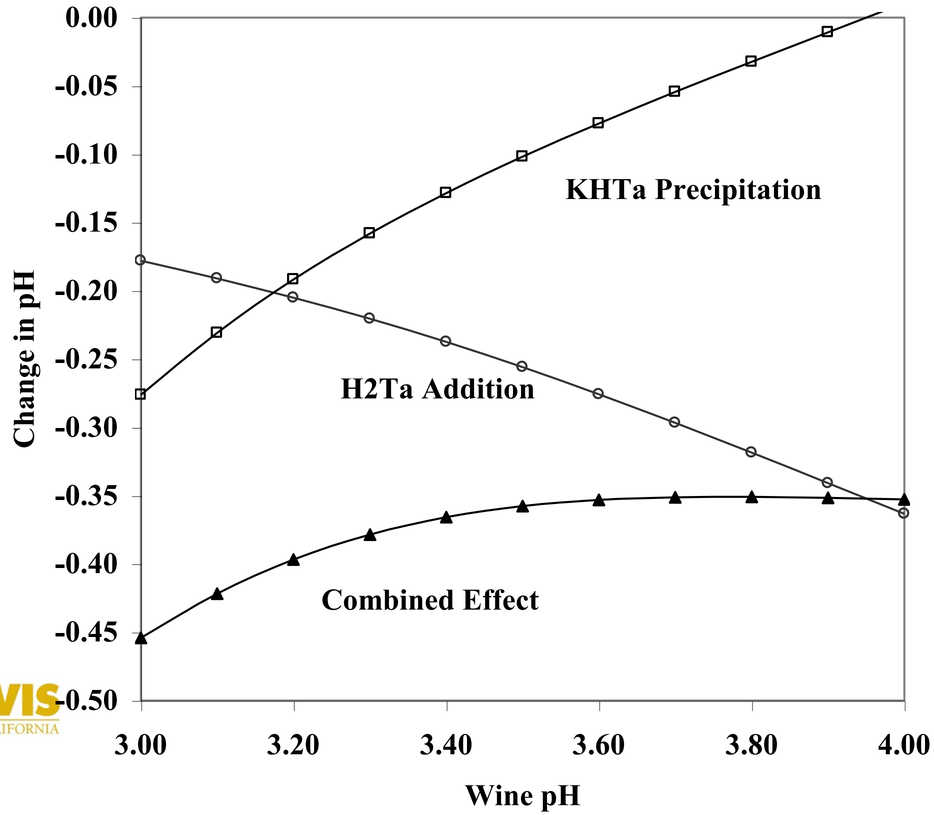
- Tartaric acid addition:
  - $H_2Ta \rightarrow H^+ + HTa^-$
  - $HTa^- \rightarrow H^+ + Ta^=$

- Release of H+ at all pHs, H+ is positive

- Precipitation of KHTa, H+ is positive, 0, or negative

$$H_2Ta \rightarrow H^+ + HTa^- \qquad HTa^- \rightarrow H^+ + Ta^=$$

Effect of H2Ta Addition and KHTa Precipitation
Model Wine, 3 g/L Addition



Levels of Potassium, Tartaric acid, pH

- Function of Temperature and %EtOH
- In Model Wines:

KHTa Solubility (g/L)

Temperature [°C]	Percent Ethanol by Volume 0%	12%	14%
0	2.25	1.11	0.98
10	3.42	1.81	1.63
20	4.92	2.77	2.51

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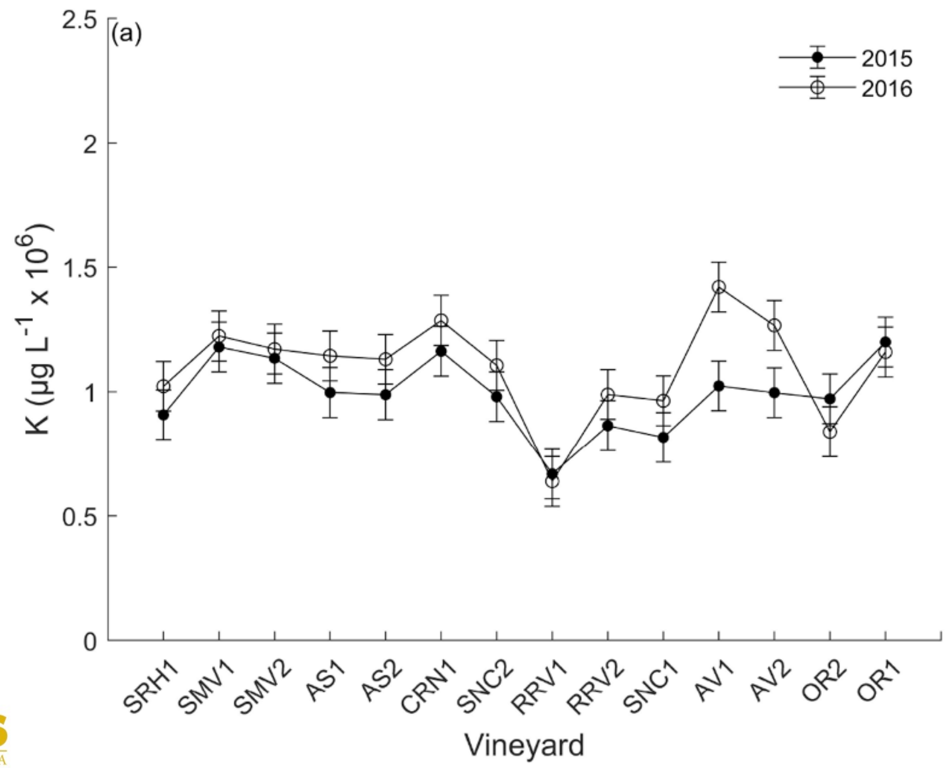
Berg, H.W. and Keefer, R.M. 1958 Am J Enol Vitic, 180-193.

Levels of Potassium in Pinot noir wines



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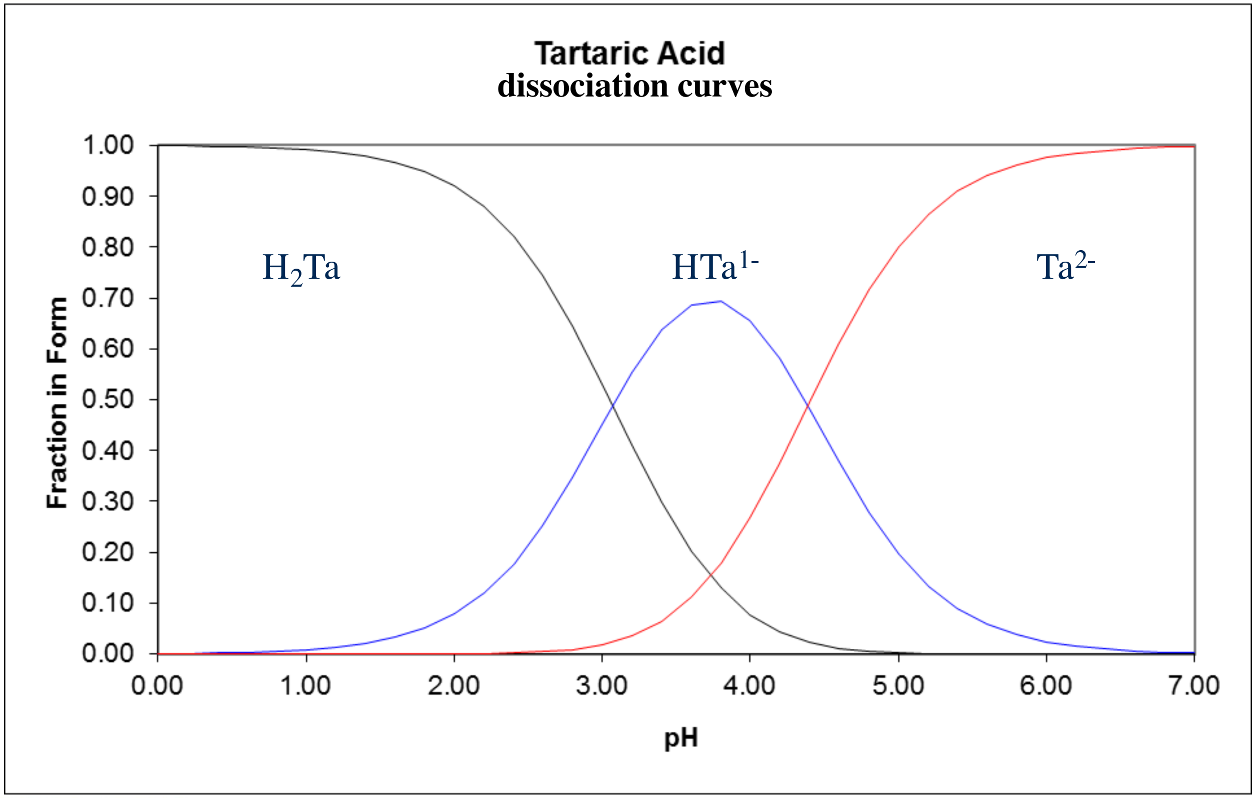
M.M.M. Lima et al., 2021. Food Research International 141 (2021) 110045

Acidity Changes during Crystallization

- KHTa
  - Loss in TA always
  - Decrease of pH if < 3.8; Increase if > 3.8
  - No change in pH if at 3.8

- CaTa
  - No loss in TA
  - Decrease in pH under all conditions

- pH change depends upon buffer capacity and extent of crystallization



$H_2Ta \rightarrow H^+ + HTa^-$ $HTa^- \rightarrow H^+ + Ta^=$

Summary

- Major acids in juice and wine
- Dissociation curves of wine components
- Potassium (K) and pH
- Titratable acidity
- pH reduction, tartaric acid additions
- pH less than 3.6 for SO_2 effectiveness during winemaking