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# Chemical Deacidifications in Winemaking

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# Acidifications and Deacidifications

## Common practices in winemaking



## Acidifications in winemaking

- Addition of acid means generally to increase the titratable acidity (TA) and/ or decrease the pH
- Frequently used in grape juices and/ or wines from warmer climates, lower latitudes, extreme warm years, lower acid varieties
- To improve the chemical health and taste balance

# Acidulants



- Chemicals used in the food industry which increase the acid and/ or decrease the pH are called “ACIDULANTS”
- They increase the acid sensation or give a prickly or tart taste
- **a) Organic Acidulants:** acetic, citric, fumaric, lactic, malic, tartaric acid
- **b) Inorganic Acidulants:** phosphoric acid

# Acidulants in winemaking

(in alphabetical order, not in order of importance)



## Calcium Sulphate ( $\text{CaSO}_4$ ) 136.4 g/mol

- Used in the production of sherry in Spain
- Legal in Canada to lower the pH in wine without increasing the titratable acid (TA)
- $\text{CaSO}_4 + \text{H}_2\text{T}$  (tartaric acid)  $\rightarrow \text{CaT} + \text{SO}_4^{2-} + 2\text{H}^+$
- The CaT precipitates, allowing a further ionization of these protons. **Lowers the pH**
- Overall pH  $\downarrow$ , TA  $\rightarrow$

# Acidulants in winemaking (cont'd)



Citric Acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) 192.14 g/mol



- Never added before fermentation
- Lactic acid bacteria can metabolize this to diacetyl and/or acetic acid
- Used in sparkling wines to prevent haze (casse)
- In Canada, **GMP** (Good Manufacturing Practices)

# Acidulants in winemaking (cont'd)



Fumaric Acid ( $\text{C}_4\text{H}_4\text{O}_4$ ) 116.07 g/mol



- Inhibitor of MLC bacteria at > 500 mg/L
- In Canada, **GMP**
- In the United States, 2.4 g/L

# Acidulants in winemaking (cont'd)



Lactic Acid ( $\text{C}_3\text{H}_6\text{O}_3$ ) 90.08 g/mol



- Used to mildly increase acid taste
- **GMP** in Canada



# Acidulants in winemaking (cont'd)



Malic Acid ( $C_4H_6O_5$ ) 134.09 g/mol



- Added as a D/L racemic mixture
- Won't precipitate like Tartaric acid (i.e. as potassium bitartrate)
- **GMP** in Canada



# Acidulants in winemaking (cont'd)



Tartaric Acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) 150.09 g/mol

$\text{COOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$

- The most common acid in winemaking
- Dissociates as follows:



# Acids in winemaking



acid	molecular weight	Kd		pKa	
		First	Second	First	Second
Tartaric acid	150.1	$9.10 \times 10^{-4}$	$4.25 \times 10^{-5}$	3.04	4.34
Malic acid	134.1	$3.50 \times 10^{-4}$	$7.90 \times 10^{-6}$	3.46	5.1
Citric acid	192.1	$7.40 \times 10^{-4}$	$1.74 \times 10^{-5}$	3.13	4.74
Succinic acid	118.1	$6.16 \times 10^{-5}$	$2.29 \times 10^{-6}$	4.21	5.64
Lactic acid	90.1	$1.40 \times 10^{-4}$		3.86	
Acetic acid	60.1	$1.76 \times 10^{-5}$		4.75	

# Deacidifications in wine



- Generally means reduction in titratable acidity (TA)
- Acid reductions are more common in northern climates and/ or cooler growing seasons
- Some acid reductions are often done systematically on certain wines (i.e. MLF on reds)

# Ameliorations



- **Both acidifications and deacidifications are sometimes called “AMELIORATIONS”:**  
To make better, improve upon, make more tolerable, amend, enhance, enrich, help meliorate, perfect, refine, upgrade
- However, in the mind of most winemakers, amelioration means use of water (dilution) to improve the wine
- Hence, amelioration has become a euphemism for “water stretching”

# Methods of Deacidification



- **Amelioration**
- **Blending**
- **Fermentation with acid reducing yeasts**
- **MLF**
  - Malo Lactic Fermentation
- **Chemical deacidification**
  - treating the juice and/ or wine with chemicals to precipitate acid

# Methods of Deacidification (cont'd)



## Amelioration

- Addition of water to juice (stretching)
- Will reduce (dilute) TA, but generally does not reduce the pH due to the buffering capacity of the juice (even if approx. 30% dilution)
- Would also require sugar additions to achieve the desired alcohol concentration
- Is used to produce mainly low alcohol products (i.e. 7% alcohol)
- Is not permitted in most countries for table wines
- Is prohibited for VQA wines (table wines)
- $TA \downarrow$ ,  $pH \rightarrow$

# Methods of Deacidification (cont'd)



## Blending

- In this context, not for flavour, rather for balance
- Blend a low acid/ high pH must or wine with one of high acid/ low pH
- Limited by
  - a) Must (juice)/ wine availability
  - b) Appellation rules (geographic indicators)
  - c) Varietal content rules
  - d) Vintage content rules
- TA↑ or↓, pH↑ or↓, depending on the wines blended



# Methods of Deacidification (cont'd)



## Fermentation with acid reducing yeast

- Small amount of Malic acid (10-20%) is degraded by some common wine yeasts (*Saccharomyces* strains)
- Using *Schizosaccharomyces pombe* (beer in Swahili), first isolated in 1893 from East African millet beer
  - First great expectations for wine, but then great disappointments
  - Needed a fairly high temperature (i.e. 32-42°C)
  - Hence it is not competitive with *Saccharomyces cerevisiae* at wine fermentation temperatures (lower)
  - Also produces off-flavours
  - Incompatible for winemaking when used as **fermenting yeast**
  - New products on market now for deacidification (See Kotseridis lecture February 15)

# Methods of Deacidification (cont'd)



## Malolactic Fermentation

- Reduces Malic acid only- converts it into Lactic acid
- Commonly used on all red wine from virtually all climates
- For a few white wines (e.g. chardonnay)



- Reduces acidity by 1-3 g/L and changes taste
- Overall :
  - TA↓, pH↑

# Methods of Deacidification (cont'd)



## Chemical Deacidifications- Chemical treatments

### a) using a weekly basic anion resin exchange

- This involves weakly bound hydroxyl groups ( $\text{OH}^-$ ) onto the exchange resin which are then exchanged for acid anions present in the wine
- The  $\text{OH}^-$  from the resin binds with the  $\text{H}^+$  proton from the wine acids to form water ( $\text{H}_2\text{O}$ ) ( $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$ )
- The acid anions from the juice/wine (i.e. sulphite, amino acids, malate, etc.) attach to the resin and stay on it. This reduces the acidity
- Overall, this process is very detrimental to quality
  - $\text{TA} \downarrow$ ,  $\text{pH} \uparrow$

# Methods of Deacidification (cont'd)



## Chemical Deacidifications- Chemical treatments

b) Potassium Tartrate ( $K_2C_6H_4O_6$ )       $K_2T$  226.27 g/mol



$$\frac{= 226.27 \text{ g/mol } (K_2T)}{150.09 \text{ g/mol } (H_2T)} = 1.5076 \sim 1.51$$

- Hence it needs 1.51 g of Pot. Titrate to remove 1.0g of Tartaric acid. The reason being because the other gram comes from the added  $K_2T$
- $K_2T$  is expensive and not very effective
- Not registered in Canada
- $TA \downarrow$ ,  $pH \uparrow$
- GMP

# Methods of Deacidification (cont'd)



## Chemical Deacidifications- Chemical treatments

### c) Carbonate Deacidifications

- Under the present and amended Canadian Food and Drug Regulations (CRC, C870, 2011-11-24)
- **Calcium Carbonate:  $\text{CaCO}_3$ , 100.09 g/mol**
  - “Simple salt” for minor deacidification
  - “Double salt” for major deacidification
- **Potassium Bicarbonate:  $\text{KHCO}_3$ , 100.12 g/mol**
  - For minor deacidification
- **Potassium Carbonate  $\text{K}_2\text{CO}_3$ , 138.21 g/mol**
  - For minor deacidification

# The chemistry involved



- Basic carbonate reactions with acids give water (H<sub>2</sub>O)+ Carbon Dioxide (CO<sub>2</sub>)



# General usage in winemaking



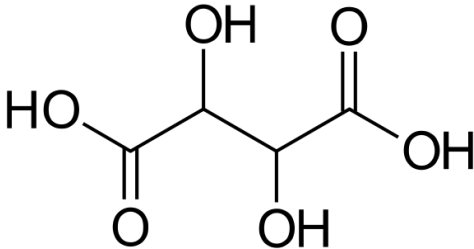
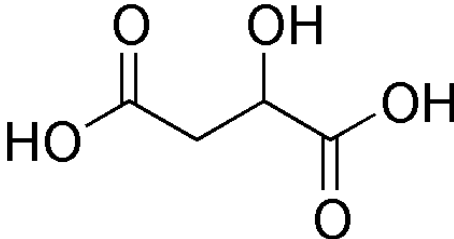
- Calcium Carbonate ( $\text{CaCO}_3$ ) has been used in winemaking for almost one hundred years
  - The two Potassium Carbonates ( $\text{KHCO}_3$ ,  $\text{K}_2\text{CO}_3$ ) have been permitted for use more recently in Europe and Canada
  - Sodium Carbonates are not permitted
    - $\text{NaHCO}_3$  (baking soda)
    - $\text{Na}_2\text{CO}_3$  (washing soda)
- (P.S. On the other hand, other sodium based chemicals such as in cation exchange or  $\text{Na}_2\text{S}_2\text{O}_5$  sodium metabisulphite are permitted)



- All “Simple” Carbonate additions- Deacidifications remove Tartaric acid only
- The double salt  $\text{CaCO}_3$  Deacidification involves both main grape acids (i.e. Tartaric acid plus Malic acid)
- All major acid adjustments (acidifications and deacidifications) are ideally performed on grape juice
- Minor adjustments are often delayed until after fermentation into the wine stage

# Acids involved in Deacidification



Tartaric Acid	Malic Acid
$C_4H_6O_6$ 150.09 g/mol	$C_4H_6O_5$ 134.09 g/mol
Several isomers	Two isomers
Only the L(+) isomer is found in grapes	Only the L(-) isomer is found in grapes
	

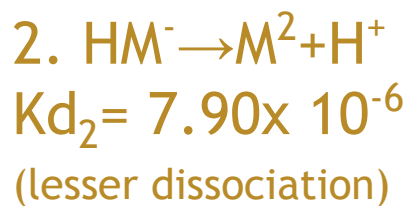
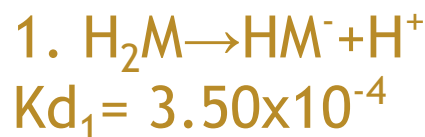
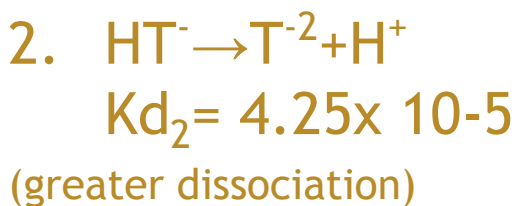
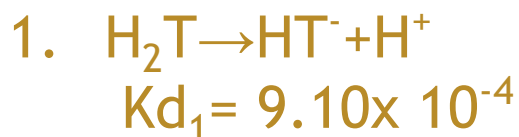
# Tartaric acid and Malic acid



- Both acids have two dissociation constants
- $K_d$  is defined as: 
$$K_d = \frac{[A^-][H^+]}{[AH]}$$

$[A^-]$  and  $[H^+]$  are the equilibrium concentration of the anionic form of the acid and its proton respectively.

$[AH]$  is the undissociated acid concentration



# Tartaric and Malic acid (cont'd)



- The greater the dissociation, the stronger the acid since the strength of an acid is a measure of its ability to release  $H^+$  ions into solutions
- The pK of a weak acid (pKa) may be defined analogously to pH or pOH
- $pKa = -\log K_d$

acid	molecular weight	Kd		pKa	
		First	Second	First	Second
Tartaric acid	150.1	$9.10 \times 10^{-4}$	$4.25 \times 10^{-5}$	3.04	4.34
Malic acid	134.1	$3.50 \times 10^{-4}$	$7.90 \times 10^{-6}$	3.46	5.1
Citric acid	192.1	$7.40 \times 10^{-4}$	$1.74 \times 10^{-5}$	3.13	4.74
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Lactic acid	90.1	$1.40 \times 10^{-4}$		3.86	
Acetic acid	60.1	$1.76 \times 10^{-5}$		4.75	

# Tartaric and Malic acid (cont'd)



Tartaric Acid	Malic acid
$pK_1 = 3.04$ (pH) $pK_2 = 4.34$ (pH)	$pK_1 = 3.46$ (pH) $pK_2 = 5.10$ (pH)

The midpoint pH between  $pK_1$  and  $pK_2$  is calculated as follows:

## Tartaric Acid

$$\frac{pK_1 + pK_2}{2}$$
$$\downarrow$$
$$\frac{3.04 + 4.34}{2} = 3.69$$

## Malic Acid

$$\frac{pK_1 + pK_2}{2}$$
$$\downarrow$$
$$\frac{3.46 + 5.10}{2} = 4.28$$

Other literature has:  $pK_1 = 2.95$   
 $pK_2 = 4.25$

$$\frac{2.95 + 4.25}{2} = 3.60$$

Therefore, the midpoint is 3.6 - 3.7

# Dissociation of Tartaric Acid

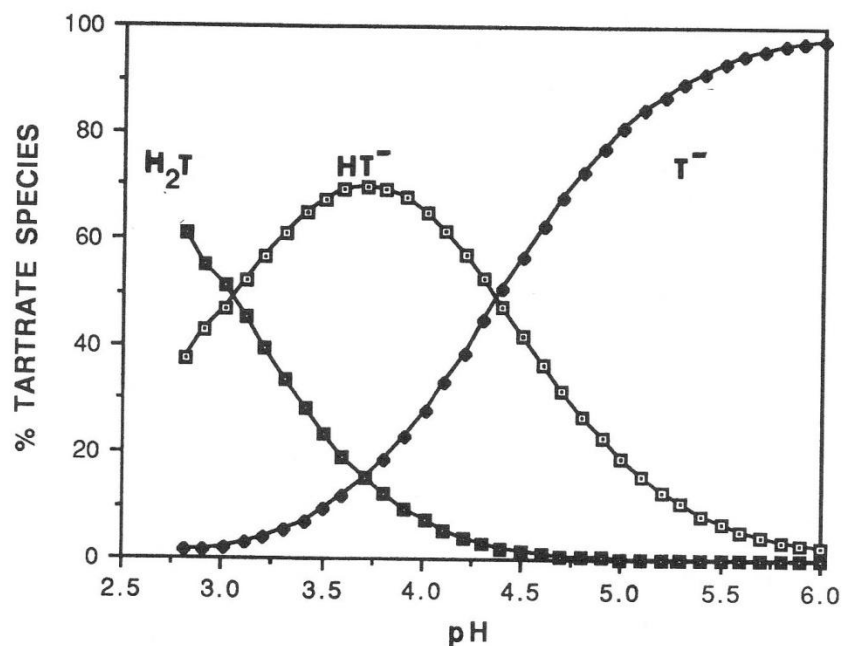
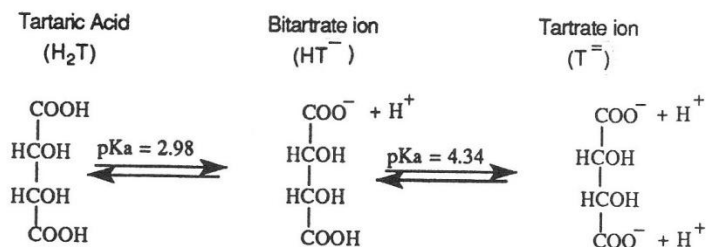
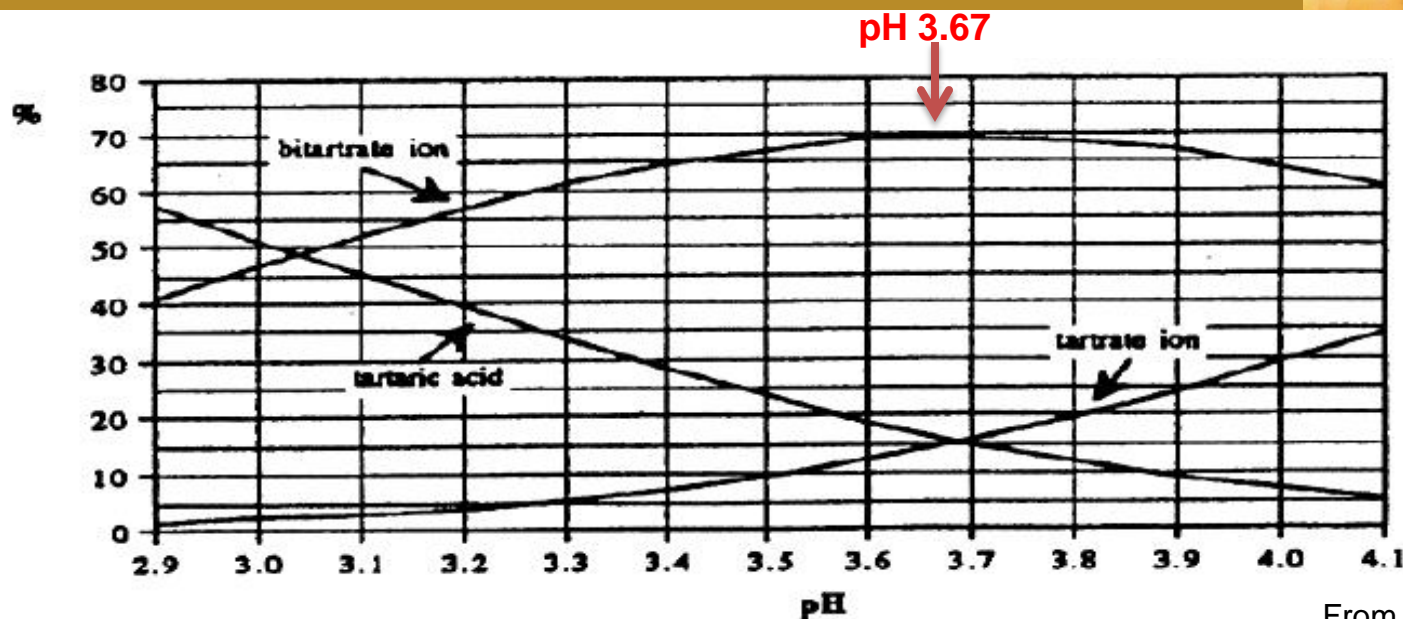


Fig. 15-1. Relative concentration of tartaric acid species in aqueous solution at different pH values.

- From Zoecklein et al, *Wine Analysis and Production*, p229



From Margalit, concepts  
in Wine Chemistry



**pH: 3.67 = maximum concentration of bitartrate ion**

when pH < 3.67, KHT ppte. causes equilibrium shift to lower pH

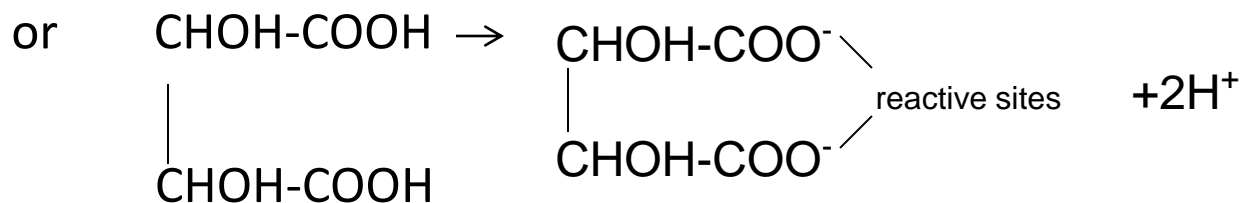
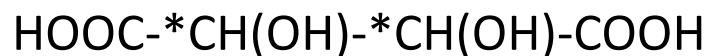
- i.e., decrease  $\text{HT}^-$ , shifts to right, produces more  $\text{H}^+$
- when pH > 3.67, KHT ppte. would increase pH
  - i.e., consumes  $\text{H}^+$  to form more  $\text{HT}^-$



# Carbonate Deacidifications (cont'd)



- All simple carbonate deacidifications remove Tartaric acid only
- Tartaric acid 150.09 g/mol

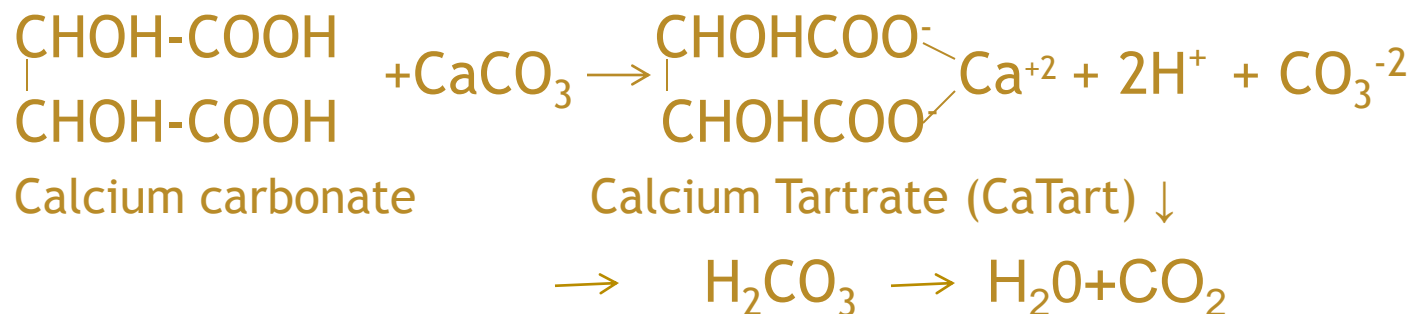


# Simple salt (Direct addition of $\text{CaCO}_3$ )



## Calcium Carbonate $\text{CaCO}_3$ 100.09 g/mol

- $\text{CaCO}_3$  in acidic environment (ie wine) dissociates
- $\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{-2}$



# Calcium Carbonate (cont'd)



- The reaction is fast initially but not complete since not all Tartaric acid is dissociated instantly
- Leaves unreacted  $\text{Ca}^{2+}$  for some time
- Needs about 6 weeks for complete calcium stability in wine
- Better and less problematic for juice deacidification since there is enough time to stabilize (fermentation time plus storage time)
- CaTart stabilizes faster at higher temperatures

# Calcium Carbonate (cont'd)



## Calculations

- Since 1.0 mol of  $\text{CaCO}_3$  reacts with 1.0 mol of Tartaric acid:

$$\frac{100.09 \text{ g/mol CaCO}_3}{150.09 \text{ g/mol Tartaric acid}} = 0.6669$$

i.e. 0.67g of  $\text{CaCO}_3$  will precipitate 1.00g of Tartaric acid

TA↓, pH↑

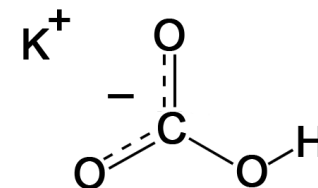
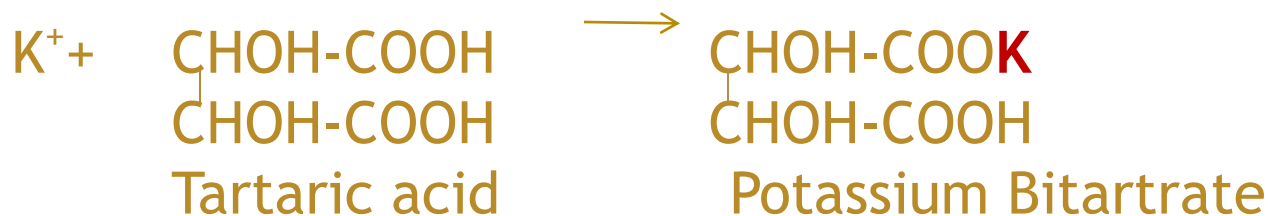
# Usage of other carbobates



## Potassium Bicarbonate $\text{KHCO}_3$ 100.12 g/mol

(Potassium Hydrogen Carbonate, Potassium acid carbonate)

- $\text{KHCO}_3$  in acidic environment (wine) dissociates



- Since 1.0 mol of  $\text{KHCO}_3$  reacts with 1.0 mol of Tartaric acid

$$\text{i.e. } \frac{100.12 \text{ g/mol KHCO}_3}{150.09 \text{ g/mol Tart. A}} = 0.6670\text{g}$$

0.67g of  $\text{KHCO}_3$  will precipitate 1.0g of Tartaric acid

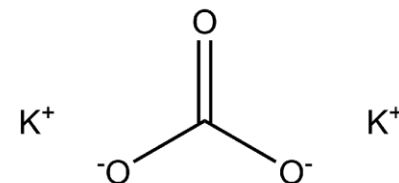
TA↓, pH↑

# Usage of other carbonates



## Potassium Carbonate $K_2CO_3$ 138.21 g/mol

- Works similar to  $KHCO_3$  but with a different stoichiometry
- For  $TA \leq 10.5$  g/L
- Since  $K_2CO_3$  has two potassium ions, only a  $\frac{1}{2}$  mol of  $K_2CO_3$  is needed to react with one mol of Tartaric acid



$$\begin{array}{l} \text{i.e. } \frac{0.5 \text{ mols} \times 138.2 \text{ g/mol } K_2CO_3}{150.09\text{g/mol Tartaric}} = \frac{0.5 \times 0.92\text{g } K_2CO_3}{1.0\text{g Tartaric}} \\ = 0.46\text{g } K_2CO_3 \rightarrow 0.46\text{g } K_2CO_3 \text{ is needed to precipitate} \\ \quad 1.0\text{g Tart} \quad \quad \quad 1.0\text{g Tartaric acid} \\ \quad TA\downarrow, pH\uparrow \end{array}$$

# Usage of other carbonates



Any addition of  $\text{KHCO}_3$  (Potassium Bicarbonate) and/or  $\text{K}_2\text{CO}_3$  will always reduce TA and increase the pH.

TA↓, pH↑

## Verifications:

- Bitartrate (KHT) in grape juice (also inside grape berries) is almost always at the saturation point (Tartaric acid: about 3.0-6.0 g/L,  $\text{K}^+$ : 1.0-2.0 g/L depending on climate, variety and vintage year)



# Factors bringing KHTart Precipitation



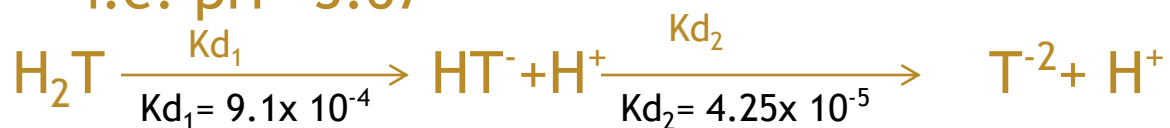
1. Prolonged storage of juice
2. Chilling of juice (the colder, the more tartrate losses-precipitates and is deposited on tank walls)
3. Formation of alcohol (fermentation) reduces solubility of potassium bitartrate
4. Chilling of wine for cold stabilization
5. Freezing the berries (Icewine making)

When bitartrate precipitates, there are changes in the medium (juice/wine)

- The acidity (TA) is always lowered
- The pH's behaviour depends on the pH value at which the KHT precipitation occurs.



- The maximum Bitartrate ion concentration  $\text{HT}^-$  happens to be at the midpoint between  $\text{pK}_1$  and  $\text{pK}_2$
- i.e.  $\text{pH} = 3.67$



$$\frac{\text{pKa}_1 (3.04) + \text{pKa}_2 (4.34)}{2} = 3.67$$

If KHT precipitation occurs at a lower pH than 3.67

(i.e.  $\text{K}^+ + \text{HT}^- \rightarrow \text{KHT}$ ), then it lowers the pH because when  $\text{HT}^-$  ppte and is lost, it triggers more  $\text{H}^+$  dissociation from  $\text{H}_2\text{T}$ ,

$\text{pH} \downarrow$ ,  $\text{TA} \downarrow$



# Consequences



If KHT precipitation occurs at a higher pH than 3.67 (i.e.  $K^+ + HT^- \rightarrow KHT$ ), then it raises the pH because when  $HT^-$  is lost when ppte forms, it triggers more  $H^+$  consumption to replenish the  $HT^-$ ,  $pH \uparrow$ ,  $TA \downarrow$

- $HT^- \leftarrow T^{-2} + H^+ \quad pK_a = 4.34$
- It is therefore advised to make roughly estimated acid corrections (acidifications or deacidifications) as early as possible at the juice stage to avoid later runaway situations (i.e. controlling the pH in red wine prior to MLF)

# Double Salt $\text{CaCO}_3$ Deacidifications



- The only Carbonate deacidification which addresses Malic acid also is the double salt precipitation with calcium carbonate
- Typical juice/ wine pH's are anywhere from pH 3.0-3.7 in Ontario climates.
- The  $\text{Ca}^{+2}$  ion will only react with the Tartaric acid and not malic acid to form CaT at this pH range



- The  $\text{Ca}^{2+}$  can not bind to Malic acid ( $\text{pK}_1 = 3.66$ ,  $\text{pK}_2 = 5.10$ ) at those pH's of 3.0-3.7 to form a precipitate
- pH needs to be raised to at least 4.5 to allow  $\text{Ca}^{2+}$  to also bind to malic acid anions and make this double salt precipitation happen

# Double Salt $\text{CaCO}_3$ Deacidifications (cont'd)



- As we can only use the  $\text{CaCO}_3$  to raise the pH to make the precipitation happen, only a fraction of the juice/wine can be used, i.e. this fraction is separated and treated with  $\text{CaCO}_3$ , the pH is then raised on this partial volume to between 4.5-6.5 by the  $\text{CaCO}_3$ , depending on the amount of  $\text{CaCO}_3$  being used
- At this higher pH, only then does some of the Malate ion react with the  $\text{Ca}^{2+}$
- Since  $\text{Ca}^{2+}$  still reacts with Tartaric acid, some “Double Salt” will be formed  
i.e. a Ca-Malate-Tartrate precipitate

# Double Salt $\text{CaCO}_3$ Deacidifications (cont'd)



- This “Double Salt” was first mentioned in 1891 by Ordonneau and later recognized by Muenz, 1960/61, that this double salt offered an opportunity to precipitate some malic acid besides tartaric acid
- In 1963, Kielhofer and Wuerdig refined this process and it was modified again in 1988 by Wuerdig
- Today, this process is recommended only for  $\geq$  TA's 11.0 g/L

# Limitations



- The Tartaric acid portion of the TA must always be  $\geq 50.0\%$ , otherwise the juice/ wine ends up with no or marginal Tartaric acid content
- Remember: Tartaric acid is a stronger acid since it is more ionized ( $K_{d1} = 9.0 \times 10^{-4}$ ,  $K_{d2} = 4.25 \times 10^{-5}$ ) than Malic acid ( $K_{d1} = 3.5.0 \times 10^{-4}$ ,  $K_{d2} = 7.9 \times 10^{-6}$ ), which accounts for the overall formation of their respective Calcium Salts
- In reality (based on their percentages present), only between 30-50% of the precipitate formed is due to the CaMalate
- Muntough (1990) showed first Malic acid would have to be twice the Tartaric level to produce a 50:50 ratio of both salts present in the precipitate

# Limitations (cont'd)



- Today, some special high purity  $\text{CaCO}_3$  salts are available which are often “doped” with 1.0% Ca Malate Tartrate crystals (as seeds) to facilitate easier crystalization (e.g. Acidex, Exacid, Malacid, Neoantacid, Sihadex)
- Several investigations cited in *Principles and Practices of Winemaking*, (1998) report less Malate removal and the 1:1 removal occurs only when the initial Malic acid was approximately twice the Tartaric acid level (Nagel et al, 1975; Munyon and Nagel 1977; Steele and Kunkee 1978, 1979)
- (P.S. However, this was in the early years and 10 years before Würdig modified the process in 1988)



# Some Double Salt Formation



pH 4.5-6.5

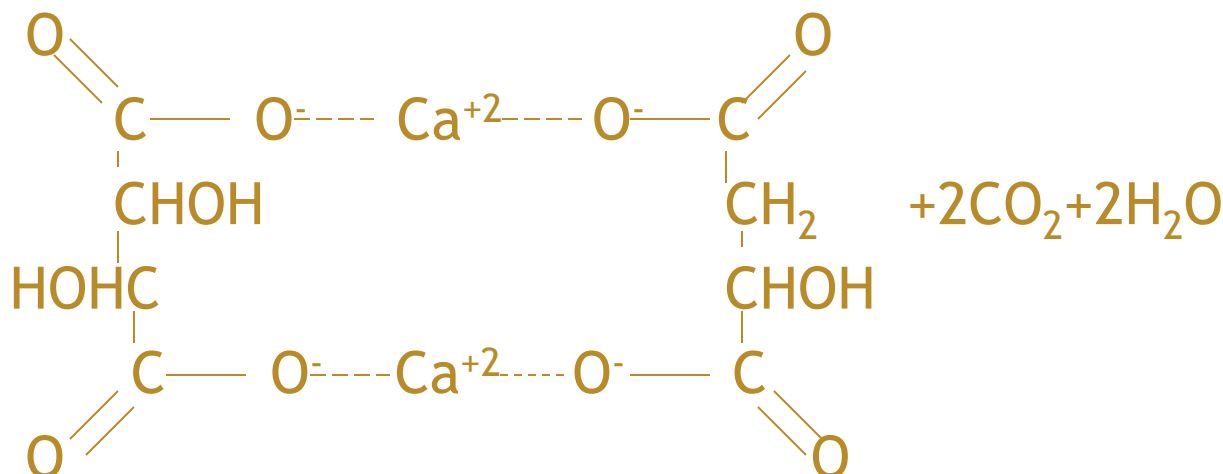
COOH-CHOH-CHOH-COOH

Tartaric Acid

+  
2CaCO<sub>3</sub>

COOH-CHOH-CHOH-COOH

Malic Acid



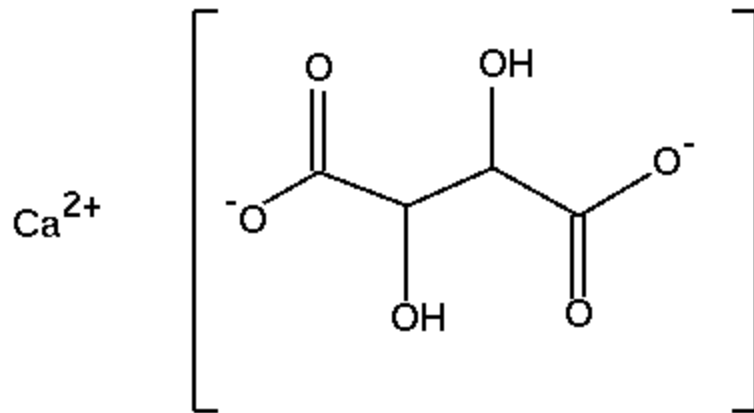
Calcium Malate Tartrate  
(Double Salt)

i.e. it takes 0.67g CaCO<sub>3</sub> to remove 1.0g of TA

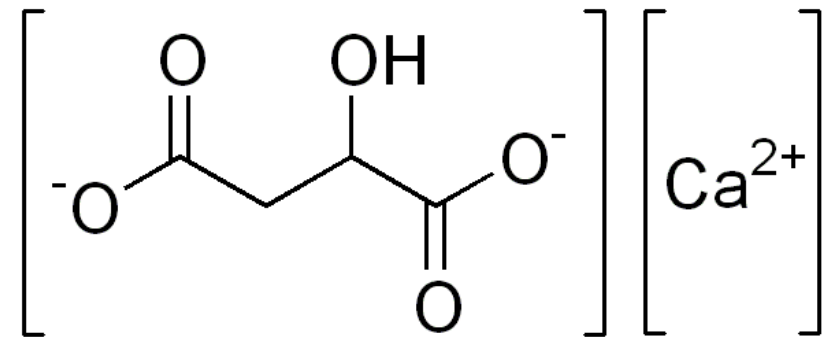
# Single Salts



## CaTartrate



## CaMalate



# Calcium Carbonate double salt precipitation



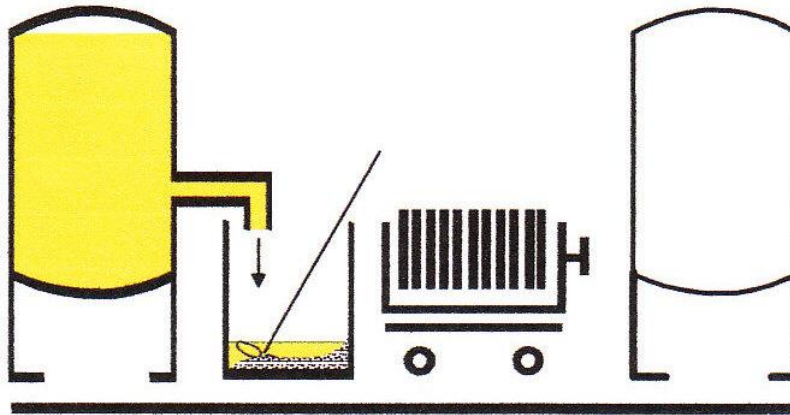
- In theory, equal molar quantities of Tartaric and Malic acid are removed- in practice, more Tartaric acid removed
  - More Tartaric vs. Malic in must/ wine
  - Calcium Tartrate can precipitate as single salt in addition to being involved in double salt precipitation
- Conditions to get a 1:1 removal of Tartaric: Malic
  - 2:1 ratio of malic: tartaric
- 2 moles of acid react with 2 moles of calcium carbonate, therefore 1:1 molar relationship
  - Mw calcium carbonate: 100g/mol, Mw Tartaric acid: 150 g/mol
  - $100/150=0.67$ , to reduce TA by 1g/L, need 0.67g/L calcium carbonate

# The process

## Step 1: Add Calcium Carbonate to Vessel



1.



**Deacidification  
vessel**

### Step 1 Adding $\text{CaCO}_3$

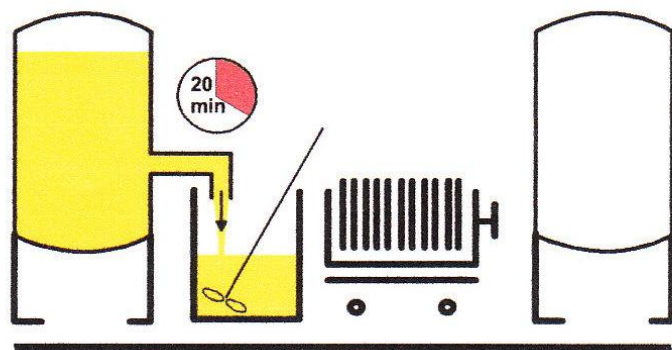
- Determine amount of calcium carbonate needed (calculation or table)
- Add the dry powder to the deacidification vessel (leave enough room for froth that develops!)
- Mix calcium carbonate thoroughly in 2-3 times the quantity of liquid

# The process

## Step 2: Add Volume of juice/wine to Calcium Carbonate



2.



Deacidification  
vessel

### Step 2 Adding juice/wine

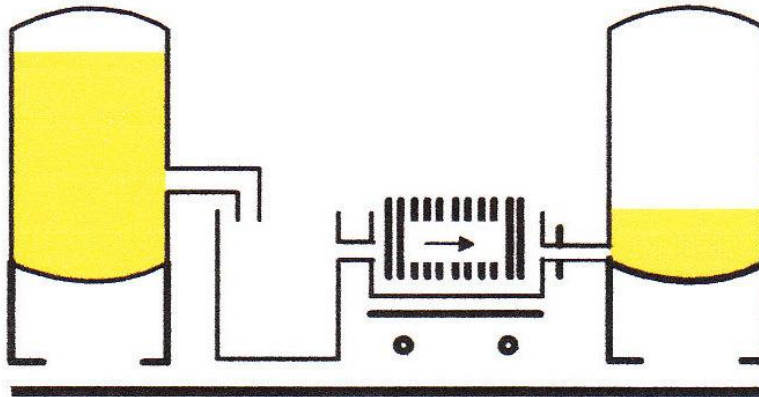
- Add the volume of juice/wine slowly to the vessel that contains the calcium carbonate to allow pH to increase to 4.5-6
- The chemistry will not work if you add the calcium carbonate to the juice/wine. Why?
- add the juice without interruption onto the blade of the agitator in the vessel
- This should take at least 20 min
- Always stir vigorously to drive out the  $\text{CO}_2$  that forms from the reaction

# The process

## Step 3: Separate the precipitated calcium salts



3.



### Step 3 Filtration

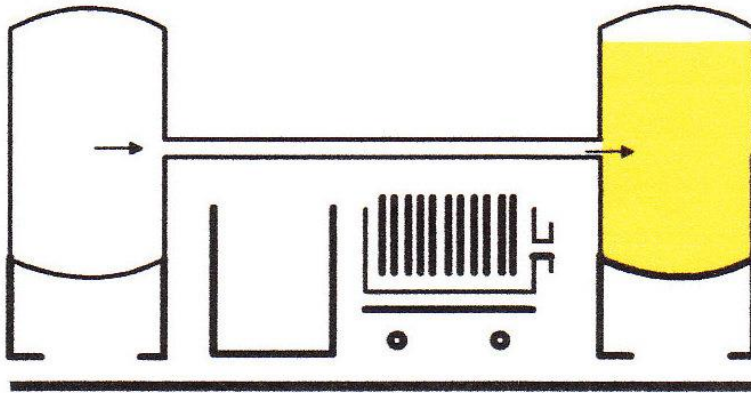
- The crystal sludge made of calcium-malate-tartrate salts must be carefully separated from the juice/wine
- Filter using course diatomaceous earth or a vacuum or yeast filter or crossflow filter

# The process

Step 4: Mix the non-deacidified juice/wine with the deacidified juice/wine



4.



## Step 4 Mixing

- Pump the non-deacidified juice/wine to the deacidified juice/wine as soon as possible and mix well

# Calculations for the Process



## 1. The following is required for this process:

- Total volume (litres) juice/wine to be treated =TV (litres)
- Total titratable acidity (g/L) = TA g/L
- Desired acid (g/L)= DA (g/L)
- Part volume (litres)= PV



# Calculations for the Process (cont'd)



## 2. Calculation of the $\text{CaCO}_3$ quantity necessary to reduce the TA for the Desired Acid Content (DAC)

$$\frac{\text{CaCO}_3 \text{ g/L}}{\text{needed}} = (\text{TA g/L} - \text{DA g/L}) \times \text{CaCO}_3 \times \text{Total Vol (L)}$$

# Calculations for the Process (cont'd)



3.a) Calculation of the Part Volume (PV) to be deacidified for juices/musts, an empirical correction factor of -2 would be applied for more accuracy

$$PV_{\text{juice}} \text{ (L)} = \frac{TA \text{ (g/L)} - DA \text{ (g/L)} \times TV}{TA \text{ g/L} - 2}$$

3.b) Calculation for the Part Volume (PV) to be deacidified for wine, an empirical correction factor of -3 would be applied for more accuracy

$$PV_{\text{wine}} \text{ (L)} = \frac{TA \text{ (g/L)} - DA \text{ (g/L)} \times TV \text{ (L)}}{TA \text{ g/L} - 3}$$

# Calculations for the Process (cont'd)



Example: TA = 15.2 g/L, DA = 8.3 g/L, Vol = 1300L

Calculation without the empirical correction factors for juice/must or wine

(Commonly textbooks do not show the correction factors)

$$\text{e.g. PV} = \frac{15.2 - 8.3}{15.2} \times 1300\text{L} = \frac{6.9 \text{ g/L} \times 1300\text{L}}{15.2 \text{ g/L}}$$

$$= 0.45 (\%) \times 1300\text{L}$$

$$= \mathbf{590} \text{ litres uncorrected}$$

590 litres uncorrected vs 680 litres for juice corrected  
or 735 litres for wine corrected

# Calculations for the Process (cont'd)



In practice, if the correction factors are not used (as in some textbooks), then there is not enough acid content in the calculated volume so that some of the  $\text{CaCO}_3$  remains unreacted and when the deacidified juice/wine is recombined with the other volume, the unreacted (residual)  $\text{CaCO}_3$  (leftover) will react only with the Tartaric acid. (i.e. reducing the tartaric acid even more so)

Results: Less Malic acid is taken out

# Calculations for the Process (cont'd)



## Recommendations:

1. Liquids (juice/wine) with  $\leq 10.5$  g/L of TA should only be deacidified with  $\text{KHCO}_3$
2. Only liquids with a TA  $\geq 11.0$  g/L should be deacidified with a Double Salt  $\text{CaCO}_3$  procedure, and even then, it might not be needed if the tartaric acid portion is significantly higher than malic acid, then  $\text{KHCO}_3$  or  $\text{CaCO}_3$  (single salt) can be used
3. If however the tartaric acid is less than the malic acid (extreme years, 19g/L TA, 12 g/L malic), then tartaric acid should be added before the double salt deacidification to bring up the ratio otherwise all tartaric acid is lost. This is called “The Malitex” process

# Icewine Surprises



- Potassium Bitrate is at its saturation point in fresh grape juice as well as inside the berry (juice)
  - Freezing of berries (temperature range  $-8.0^{\circ} \rightarrow -14.0^{\circ} \text{C}$ ) KHT (Bitartrate) precipitates in the berry.
    - The colder, the more precipitation, the more loss
  - Loss of Tartaric acid, drop in acidity (TA)
  - Malic acid is not precipitated (i.e. none is lost in the berries)
  - Upon pressing, the concentrated juice retains most of the Malic acid, calcium and nutrients
- (i.e at 40.0 Brix ( $-10^{\circ} \text{C}$ ), volume is halved, the Malic acid is typically doubled (from 2.0 up to 4.0 g/L) and so is the calcium since these are always recovered in the Icewine juice

# Chemical composition of 298 Vidal Icewine juices from the 2003 and 2004 vintages in the Niagara Peninsula



	<b>Soluble Solids (°Brix)</b>	<b>Yeast Assimilable Amino Acid Nitrogen (mg N /L)</b>	<b>Ammonia Nitrogen (mg N/L)</b>	<b>Total Yeast Assimilable Nitrogen (mg N/L)</b>	<b>pH</b>	<b>Titratable Acidity (g/L tartaric acid)</b>	<b>Malic Acid (g/L)</b>
<b>Avg</b>	<b>39.3 ± 1.7</b>	<b>498 ± 105</b>	<b>57 ± 19</b>	<b>555 ± 120</b>	<b>3.38 ± 0.16</b>	<b>10.5 ± 1.5</b>	<b>7.8±1.3</b>
<b>Low Value</b>	<b>32.0</b>	<b>182</b>	<b>6</b>	<b>188</b>	<b>2.96</b>	<b>7.0</b>	<b>4.9</b>
<b>High Value</b>	<b>46.1</b>	<b>738</b>	<b>118</b>	<b>846</b>	<b>3.98</b>	<b>14.6</b>	<b>11.0</b>

Inglis, Kaiser, Kontkanen, and Quai, unpublished

# Icewine (cont'd)



- Malic acid is usually very dominant in Iceswine juices
- If the pH of the berry juice was below pH 3.67 in the berry, then the loss of Tartaric acid, left behind in the berry in the form of KHT, lowers the pH and TA in Iceswine juices
- It is sometimes observed that the TA in Iceswine juices is actually lower than in the original juice before freezing, even though concentration had occurred but because most of the bitartrate had precipitated, the TA was lowered.
- Acid additions rather than deacidifications might be necessary and can be tricky!





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# Thank You!

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