14.12.1: Foods- Calcium Tartrate and Treatment of Wine Waster-Waters

Tartaric acid (TA) is a byproduct of wine production. This organic acid and its salts are used in foods such as fruit jellies, preserves, jams, baked goods, and confections. TA is hardly metabolized and degraded by yeast and spoilage bacteria providing microbiological stability to foods that contain it. In addition to its use as antimicrobial and acidulant, TA and its salts are used as emulsifiers, leavening, and anticacking agents.[1] TA is also used in the beverage industry and has non-food uses in textile coloring, galvanizing, and mirror production.

The increasing popularity in wine consumption in recent years has resulted in the increase of waste from wine making practices.[2] One liter of white wine generates the same amount of water pollution as 3 people in one day.[3] Waste-waters from wine production contain biodegradable compounds and fruit suspended solids; [4] their treatment is of great importance because their high pollutant activity. Moreover, waste treatment is of economic interest because the organic compounds present in waste from the wine making process can have value as additives, ingredients, and substrates in the food and pharmaceutical industries.

Waste derived from wine making

Type of Waste	Name	Derived from	Treatment[3]
Liquid/Sludge	Vinasse	Vintage process	Anaerobic digestion, ozonation, thermophilic anaerobic digestion, aerobic biodegradation, sequencing batch reactor, electrodialysis, and wet oxidation
Solid waste	Grape marc	Skin, stalks, and seeds	Combustion, solid-state fermentation, incineration, composting, and pyrolysis.
	Vine shoots	Vine pruning	
	Lees	Grapes and yeast	

Tartaric Acid separated from grape juice

Tartaric Acid crystals

The table above shows sources of waste in wine making as well as methods to treat them. A method devised by Rivas, et al. (2006) to treat distilled lees involves the reaction of tartaric acid with calcium-ions to form calcium tartrate. This salt of limited solubility is then redissolved with HCL to obtain TA. Upon removal of TA, the distilled lees can be used as nutrients for lactic acid bacteria (*Lactobacilllus pentosus*) for production of lactic acid.

In the method described above, addition of calcium ions prompts the precipitation of calcium tartrate. Once tartaric acid is removed from the solution as tartrate, it will partially dissociate into calcium and tartrate ions establishing the following equilibrium with the solid salt:

$$CaC_4H_4O_6(s) \rightleftharpoons Ca^{2+}(aq) + C_4H_4O_6^{2-}(aq)$$ with the corresponding equilibrium constant $K_{sp} = [Ca^{2+}][C_4H_4O_6^{2-}] = 7.7 \times 10^{-7} \, mol^2 dm^{-6}$ If we designate as *x* the concentration of each of the ions, the concentration of calcium-ions at equilibrium is

$$x^2 = 7.7 \times 10^{-7} \, mol^2 dm^{-6} \tag{14.12.1.1}$$

From which $x = \sqrt{7.7 \times 10^{-7} \, mol^2 dm^{-6}} = 8.77 \times 10^{-4} \, mol \, dm^{-3}$ The concentration of calcium-ions at equilibrium is 8.77 x 10^{-4} mol dm^{-3}. If now we increase the concentration of tartrate-ions, the equilibrium will shift to the *left* according to the Le Chatelier's principle. More calcium tartrate will precipitate, decreasing the concentration of calcium ions. The decrease in concentration obtained in this way is often referred to as the **common-ion effect**. Similarly, if an excess of calcium-ions is added to the solution, the concentration of tartrate-ion will decrease. Since in this process we are concerned about removing as much tartaric acid in the form of tartrate as possible, addition of calcium ions in excess will minimize dissociation of calcium tartrate increasing its the yield. The solubility product can be used to calculate how much the calcium-ion concentration is decreased by the common-ion effect. Suppose we mix 10 cm^3 of a saturated solution of calcium tartrate with 10 cm^3 of concentrated sodium tartrate (4 *M* C$_4$H$_6$O$_6$). Because of the twofold dilution, the concentration of tartrate will be 2 mol dm^{-3}. Feeding this value into equation 7 from the solubility product section, we then have the result or $7.7 \times 10^{-7} \, mol^2 dm^{-6} = [Ca^{2+}](2 \, mol \, dm^{-3})$ so that $[Ca^{2+}] = \frac{7.7 \times 10^{-7} \, mol^2 \, dm^{-6}}{2 \, mol \, dm^{-3}} = 3.85 \times 10^{-7} \, mol \, dm^{-3}$ We have thus lowered the calcium-ion concentration from an initial value of 8.77 x 10^{-4} mol dm^{-3}) to a final value of 3.85 × 10^{-7} mol dm^{-3}, a decrease of about a factor of 2000!.

Because it tells us about the conditions under which equilibrium is attained, the solubility product can also tell us about those cases in which equilibrium is *not* attained. If extremely dilute solutions of $Na_2C_4H_6O_6$ and $CaCl_2$ are mixed, for instance, it may be that the concentrations of calcium ions and chloride ions in the resultant mixture are both too low for a precipitate to form. In such a case we would find that the product Q, called the ion product and defined by

$$Q = (c_{Ca^{2+}})(c_{C_4H_4O_6^{2-}}) \ (1)$$

In this case Q has a value below the solubility product, 7.7×10^{-7} mol^2 dm^{-6}. In order for equilibrium between the ions and a precipitate to be established, either the calcium-ion concentration or the tartrate-ion concentration or both must be increased until the value of Q is exactly equal to the value of the solubility product. The opposite situation, in which Q is larger than K_{sp}, corresponds to concentrations which are too large for the solution to be at equilibrium. When this is the case, precipitation occurs, lowering the concentration of both the lead and chloride ions, until Q is exactly equal to the solubility product. To determine in the general case whether a precipitate will form, we set up an ion-product expression Q which has the same form as the solubility product, except that the *stoichiometric* concentrations rather than the *equilibrium* concentrations are used. Then if

$Q > K_{sp}$ precipitation occurs

while if $Q < K_{sp}$ no precipitation occurs

EXAMPLE 1 Decide whether CaC_2O_4, calcium oxalate, will precipitate or not when (a)100 cm^3 of 0.02 M $CaCl_2$ and 100 cm^3 of 0.02 M $Na_2C_2O_4$ are mixed, and also when (b) 100 cm^3 of 0.0001 M $CaCl_2$ and 1000 cm^3 of 0.0001 M $Na_2C_2O_4$ are mixed. K_{sp} = 2.32×10^{-9} mol^2 dm^{-6}.

Solution

a) After mixing, the concentration of each species is halved. We thus have $c_{Ca^{2+}} = 0.01$ mol $dm^{-3} = c_{C_2O_4^{2-}}$ so that the ion-product Q is given by $Q = c_{Ca^{2+}} \times c_{C_2O_4^{2-}} = 0.01$ mol $dm^{-3} \times 0.01$ mol dm^{-3} or $Q = 10^{-4}$ $mol^2 dm^{-6}$

Since Q is larger than K_{sp} (2.32×10^{-9} mol^2 dm^{-6}), precipitation will occur.

b) In the second case the concentration of each ion becomes $c_{Ca^{2+}} = \frac{0.0001 \text{ mol dm}^{-3} \times 100 \text{ cm}^3}{1100 \text{ cm}^3} = 9.09 \times 10^{-6} \text{mol dm}^{-3}$ and $c_{C_2O_4^{2-}} = \frac{0.0001 \text{ mol dm}^{-3} \times 1000 \text{ cm}^3}{1100 \text{ cm}^3} = 9.09 \times 10^{-5} \text{mol dm}^{-3}$

thus

$$Q = c_{Ca^{2+}} \times c_{C_2O_4^{2-}} \tag{14.12.1.2}$$
$$= (9.09 \times 10^{-6} \text{mol dm}^{-3})(9.09 \times 10^{-5} \text{mol dm}^{-3}) \tag{14.12.1.3}$$
$$= 8.26 \times 10^{-10} \text{mol}^2 \text{dm}^{-6} \tag{14.12.1.4}$$

Since Q is now less than K_{sp}, no precipitation will occur.

EXAMPLE 2 Calculate the mass of CaC_2O_4 precipitated when 100 cm^3 of 0.0200 M $CaCl_2$ and 100 cm^3 of 0.0200 M $Na_2C_2O_4$ are mixed together.

Solution In in part *a* of the previous example we determined that precipitation does actually occur. In order to find how much calcium oxalate is precipitated, we must concentrate on the amount of each species. Since 100 cm^3 of 0.02 M $CaCl_2$ was used, we have

$n_{Ca^{2+}} = 0.0200 \frac{\text{mmol}}{\text{cm}^3} \times 100 \text{ cm}^3 = 2.00 \text{ mmol}$

similarly $n_{C_2O_4^{2-}} = 0.0200 \frac{\text{mmol}}{\text{cm}^3} \times 100 \text{ cm}^3 = 2.00 \text{ mmol}$ If we designate the amount of CaC_2O_4 that precipitates as *x* mmoles, we can set up the following table

Species	Ca^{2+} *(aq)*	$C_2O_4{}^{2-}$ *(aq)*
Initial amount (mmol)	2.00	2.00

Amount reacted (mmol)	$-x$		$-x$	
Equilibrium amount (mmol)	$(2-x)$		$(2-x)$	
Equilibrium concentration (mmol cm^{-3})	$\frac{2-x}{200}$		$\frac{2-x}{200}$	

Thus

$$K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

or $\qquad 2.32 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6} = \left(\frac{2-x}{200} \text{ mol dm}^{-3}\right)\left(\frac{2-x}{200} \text{ mol dm}^{-3}\right) \qquad$ Rearranging,

$200^2 \times 2.32 \times 10^{-9} = 9.28 \times 10^{-3} = (2-x)^2$ or $2-x = \sqrt{9.28 \times 10^{-3}} = 0.096$ so that $x = 2 - 0.096 = 1.904$ Since 1.904 mmol of CaC$_2$O$_4$ precipitated, its mass is

$$m_{\text{CaC}_2\text{O}_4} = 1.904 \text{ mmol} \times 146.11 \frac{\text{mg}}{\text{mmol}} \qquad (14.12.1.5)$$

$$= 278.2 \text{ mg} = 0.278 \text{ g} \qquad (14.12.1.6)$$

Note: Since the solubility product of CaC$_2$O$_4$ is very small, about 95% of the calcium oxalate originally formed precipitates.

References

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