Acid–Base and Precipitation Equilibria in Wine

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One goal of the introductory analytical chemistry course at the University of Cádiz is to provide an understanding of the concepts of equilibrium and conditional equilibrium to chemistry, chemical engineering, and enology students. Typically the concept of acid–base equilibrium is taught first, followed by the equilibria of precipitation, oxidation–reduction, and complexation. As more types of equilibria are introduced, the processes studied become increasingly complex owing to the consideration of more systems *(1).*

For the enology degree, knowledge is required of the chemical equilibria applicable to wine and related products, such as vinegar and distillates. All are acid products with, in most cases, a pH lower than 4 owing to the presence of tartaric or acetic acid. The pH conditions dictate the chemical processes taking place in wine.

The precipitation of potassium hydrogen tartrate is the most important of the processes that adversely affect the stability of wine (Scheme I). In most cases, wine can be viewed as an oversaturated solution of potassium hydrogen tartrate. This over-saturation is maintained as a result of the formation of complexes not only between the tartaric acid and the other compounds present in the wine, such as phenolic-type compounds and other organic acids *(2),* but also between the potassium and these other compounds.

A normal concentration range of K^+ in wine is 0.5–1.5 g/L where as the total tartaric acid concentration is normally between 0.8 and 2.0 g/L. Consequently, the product of concentrations for potassium hydrogen tartrate is usually established between 0.27 g^2/L^2 and 2.01 g^2/L^2 (i.e., between 4.6×10^{-5} and 3.4×10^{-4} mol^2/L^2) for a wine with pH = 3.5 in which approximately 67% of the tartaric acid is found in the form of hydrogen tartrate. Similarly, the solubility product in an aqueous medium at 25 °C is 5×10^{-5} mol^2/L^2 for potassium acid tartrate.

To avoid precipitation occurring once the wine has been bottled, producers usually chill the bulk wine in tanks down to temperatures between −2° and 5 °C for a period of 2–10 days *(3).* Partial precipitation of potassium hydrogen tartrate is achieved as a result of the decrease in magnitude of the solubility product at lower temperature. In this way, the condition of over-saturation is reduced, stabilizing the wine against the occurrence of this phenomenon.

The pH variation during the precipitation of the potassium hydrogen tartrate is due to the presence of three related species: tartaric acid, hydrogen tartrate, and tartrate. Of the three, only the hydrogen tartrate precipitates with potassium. Its concentration decrease during the precipitates causes the acid–base equilibria of the related species to be displaced.

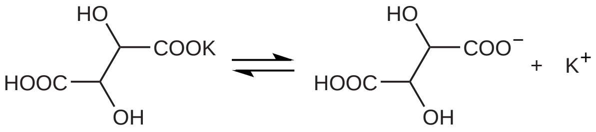
The variation in the pH is related to the initial quantity of each of the three species, as well as to the values of the equilibrium constants of the two equations shown in Schemes II and III. The equilibrium constants are 9.12×10^{-4} and 4.26×10^{-5}, respectively, in aqueous solution *(4).*

The pH of maximum concentration of the hydrogen tartrate species is 3.70. At this pH value the concentrations of tartaric acid and tartrate are equal. Therefore if the precipitation occurs at or close to this point, the variation in pH will be minimum or nonexistent. In contrast, if the precipitation occurs at lower pH values, the higher relative concentration of the tartaric acid will cause the equilibrium in Scheme II to be the major contributor to the formation of the hydrogen tartrate. Therefore as precipitation occurs the simultaneous generation of protons from this equilibrium will make the pH decrease.

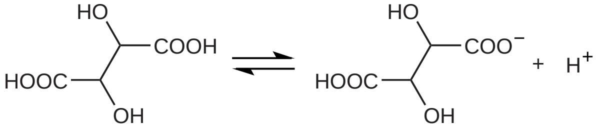
In an analogous way, if the precipitation takes place at pH values higher than 3.70, the higher relative concentration of tartrate and the equilibrium in Scheme III will dominate. The precipitation of hydrogen tartrate will produce an increase in pH as a result of the protons reacting with tartrate to generate hydrogen tartrate.

Experimental Overview

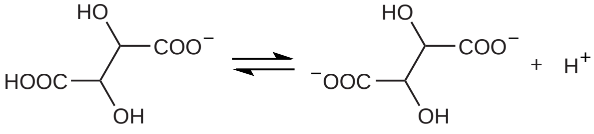
The experiments consist of determining the changes of pH during the precipitation of potassium hydrogen tartrate from aqueous solutions or from wine samples. To hasten the precipitation process, a solution is cooled from approximately 50 °C down to ambient temperature. This process is the same as that which occurs during the stabilization of a wine, except that in this experiment a different temperature range is



Scheme I. Precipitation equilibrium for potassium hydrogen tartrate.



Scheme II. Acid–base equilibrium I: tartaric acid and hydrogen tartrate.



Scheme III. Acid–base equilibrium II: hydrogen tartrate and tartrate.

used. Sodium tartrate is used to generate tartaric acid, hydrogen tartrate, and tartrate. Hydrochloric acid is used to establish the desired pH.

Experiment 1

Adjust the pH of a solution of 1 g of sodium tartrate dissolved in 25 mL of H_2O to 3.2 with a HCl solution (0.1–0.5 M). While continuously stirring, add 1 g of potassium chloride to the solution of sodium tartrate, preheated to 50 °C. Record the pH and temperature every 30 seconds as the solution cools.

Experiment 2 and 3

Adjust the pH of a solution of 1 g of sodium tartrate dissolved in 25 mL of H_2O to 4.2 or 3.7, respectively, with a HCl solution (0.1–0.5 M). While continuously stirring, add 1 g of potassium chloride to the solution of sodium tartrate, preheated to 50 °C. Record the pH and temperature every 30 seconds as the solution cools.

Experiment 4 and 5

While continuously stirring, add 2 g of potassium chloride to 25 mL of a white wine sample or to 25 mL of a red wine sample, respectively. Both samples should be preheated to 50 °C. Record the pH and temperature every 30 seconds as the solution cools.

Hazards

Standard precautions should be taken when handling acids and bases.

Results

The variations of pH and temperature with time in the experiments described above are shown in Figures 1–3. When the initial pH is less than 3.7, the pH falls below its initial level as the solution cools (Figure 1). This is due to the precipitation of the potassium hydrogen tartrate. Equilibrium I (Scheme II) is displaced towards the right to a greater extent than the displacement of equilibrium II (Scheme III). In contrast when the initial pH is greater than 3.7, the pH increases proportional to the reduction of temperature as a result of the precipitation (Figure 2). Finally, in the case of the solution with an initial pH close to 3.7, it can be seen that the variation of pH is clearly not proportional to the reduction of temperature (Figure 3); the changes in pH are minimal.

It must be noted that the solution pH of maximum concentration of hydrogen tartrate anion in the case of wine may be different from pH of 3.7 owing to the equilibrium constants being different in wine as compared to an aqueous solution. This is due to the presence of ethanol.

It is important to emphasize that, in the case of the experiment conducted with an initial pH less than 3.7, an increase of the concentration of protons is produced while a decrease of the quantity of total acid in solution is observed. The student must understand that when dealing with weak acids, a lower concentration of acid in solution does not necessarily mean an increase of pH. When the decrease is due to the disappearance of the species that presents a low con-

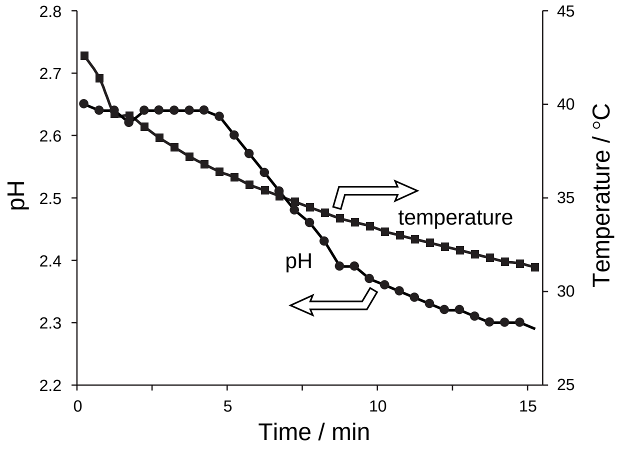


Figure 1. Variation of pH and temperature with time in an aqueous solution with an initial pH less than 3.7.

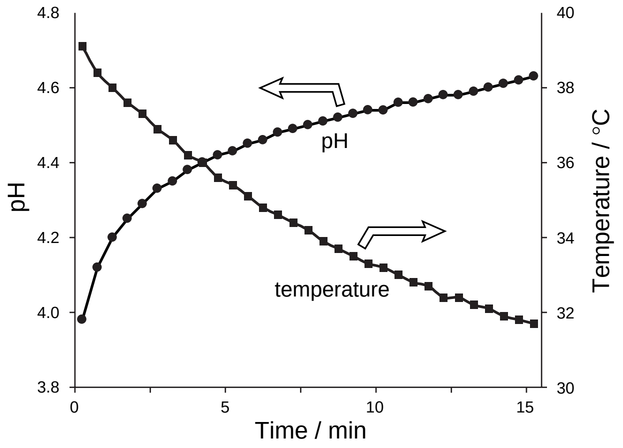


Figure 2. Variation of pH and temperature with time in an aqueous solution with the initial pH greater than 3.7.

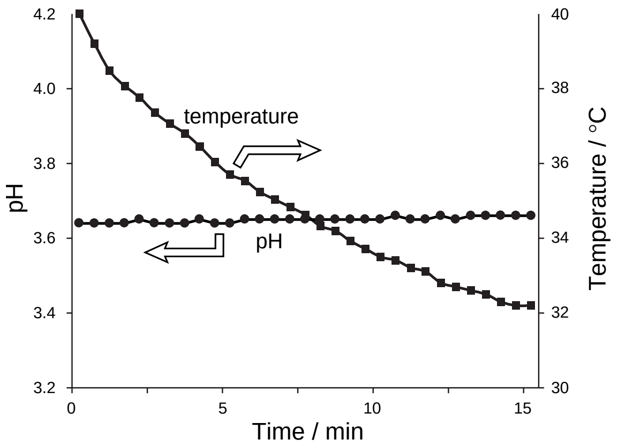


Figure 3. Variation of pH and temperature with time in an aqueous solution with an initial pH near 3.7.

stant of acidity, its regeneration from the more acidic species can involve a net increase of the concentration of protons.

The experiments run with wines can demonstrate to the students the application of the conditional equilibria in real-world samples. The different initial pH of white and red wines (usually lower in white wines) produce different pH changes when the precipitation occurs in both wines.

Conclusion

In participating in these experiments, students gain a better understanding of the variation of pH with precipitation, enabling them to better understand the interactions that take place between the different types of chemical equilibria within a single medium. These experiments were performed during the laboratory classes of the enological chemistry and enological chemical analysis and control courses forming part of the first course of the enology degree program taught by the University of Cádiz. Participation in these experiments translated into a better understanding of the equilibrium process on the part of our students, as shown by the answers to the postlab questions.

WSupplemental Material

Instructions for the students, prelab and postlab questions, and notes for the instructor are available in this issue of *JCE Online*.

Literature Cited

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