OXYGEN UPTAKE IN WINE

by

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When wine is exposed to excessive amounts of air, some of the alcohol becomes oxidized. The color of the wine becomes deeper, and the wine takes on a sherry-like characteristic. Although prized in sherry wines, these oxidized smells and flavors are considered major flaws in table wines. Oxidation spoils significant amounts of wine each year. Therefor, protecting wine from oxidation is an important consideration in every winery. Some oxygen is always dissolved in wine during cellar operations like racking, filtering, bottling, etc. and when handled under adverse conditions, wine becomes saturated with oxygen quickly. About twice as much oxygen can dissolve in cold wine (32 F), compared to wine at room temperature, so considerable care must be taken when handling wines during cold stabilization.

Dissolved Oxygen

Gases dissolve in liquids. The gas molecules occupy space between the liquid molecules, and liquids become saturated with gas when all of the space is gone. When a liquid becomes saturated, no more gas can dissolve in the liquid. Liquids become saturated with gas quickly when large surface areas are exposed to air. Air contains about 21 percent oxygen, and when wine is exposed to air, oxygen dissolves in the wine. The quantity of dissolved gas depends on the partial pressure of the gas and the temperature of the liquid. Saturated water at room temperature contains about 10 milligrams of oxygen per liter. Saturated wine contains about 7 milligrams of oxygen per liter.

Dissolved oxygen diffuses through wine until other organic molecules are encountered. Some of the molecules encountered react with the oxygen but most wine materials do not. When oxygen reacts with wine materials, new oxygen containing compounds are formed, and dissolved oxygen is removed from the liquid. But, many of these oxidation reactions occur very slowly, so much time may be required for dissolved oxygen to disappear from the wine. Depending on storage conditions, several days to several weeks may be required before all of the dissolved oxygen is consumed by these chemical reactions. So, oxygen uptake occurs quickly, but dissolved oxygen disappears slowly under normal winemaking conditions.

Too much oxygen directly affects wine quality, so winemakers must guard against excessive oxygen pickup from crush until bottling time. Understanding how oxygen is introduced and interacts with wine can help winemakers avoid wine oxidation problems.

Alcohol Oxidation

When wine oxidizes, some alcohol is converted into a material called acetaldehyde. Acetaldehyde is a volatile liquid with a nut-like odor. Acetaldehyde gives Sherry much of its distinctive character. However, alcohol does not oxidize readily, and the conversion into acetaldehyde involves a two-step process. First, oxygen interacts with phenolic compounds in the wine. Hydrogen peroxide (H_2O_2) is produced as a byproduct and hydrogen peroxide is a strong oxidizing agent. Second, hydrogen peroxide then interacts with alcohol (CH_3CH_2OH) and produces acetaldehyde (CH_3CHO) and water (H_2O). The alcohol and hydrogen peroxide reaction can be characterized as:

$$CH_3CH_2OH \quad + \quad H_2O_2 \quad =========> \quad CH_3CHO \quad + \quad 2H_2O$$

The production of hydrogen peroxide in the first step is of interest to winemakers because sulfur dioxide and hydrogen peroxide react readily and form sulfuric acid (H_2SO_4). Of course in an aqueous solution, sulfuric acid occurs as sulfate ions (SO_4^{2-}).

Wine contains about 100 grams of alcohol per liter and only about 0.1 grams of sulfur dioxide per liter. However, hydrogen peroxide and sulfur dioxide have an affinity for each other, and much of the hydrogen peroxide produced in the first wine oxidation step reacts with sulfur dioxide rather than alcohol. By that means, small quantities of sulfur dioxide in wine convert much of the oxygen into sulfate ions before the oxygen can react with alcohol and produce acetaldehyde.

Sulfur Dioxide-Oxygen Reactions

Oxygen is introduced when wine is racked, filtered, bottled, etc. In fact, some oxidation occurs anytime wine is handled, and one of the most important reasons for adding sulfur dioxide is to scavenge oxygen. Some of the added sulfur dioxide reacts with water (H_2O) and forms bisulfite (HSO_3^{1-}) and sulfite (SO_3^{2-}). A small part remains as molecular sulfur dioxide (SO_2) in the wine.

$$SO_2 + H_2O \quad \text{<=========>} \quad H^{1+} + HSO_3^{1-} \quad \text{<=========>} \quad 2H^{1+} + SO_3^{2-}$$

The sulfite then reacts with oxygen and produces sulfate.

$$2SO_3^{2-} + O_2 \quad \text{========>} \quad 2SO_4^{2-}$$

These equations show how two sulfur dioxide molecules react with one oxygen molecule to form two sulfate ions. The molecular weight of sulfur (S) is 32 and oxygen (O) is 16, so the molecular weight of SO_2 is 32 + 16 + 16 = 64. Since the weight of SO_2 is 64 and the weight of oxygen is 16, four milligrams of sulfur dioxide is required to react with one milligram of oxygen. Knowing that 4 milligrams of sulfur dioxide removes one milligram of oxygen is a handy tool.

The free sulfur dioxide content slowly decreases as wine ages. Some SO_2 is consumed as it reacts with oxygen, and some free SO_2 reacts and becomes bound SO_2 . The depletion rate of sulfur dioxide depends primarily on storage conditions. Wines stored in cool cellars and in large tanks with minimum headspace may lose about 5 milligrams of free SO_2 per liter in a month. On the other hand, wine stored in warm cellars, in small partially filled and frequently opened containers may lose 20 or more milligrams of free SO_2 per liter in a month. Free sulfur dioxide losses can be substantial during warm weather, so many wineries test and add sulfur dioxide to their wines once a month.

Oxygen and Yeast Development

Yeast requires oxygen early in the fermentation process to reproduce new cells. Most yeast strains need about 10 milligrams of oxygen per liter to produce a large, healthy yeast population. Not enough cells develop when yeast lacks oxygen, and fermentation can then be sluggish or even stop. (Sometimes, just racking and splashing the must to introduce a new supply of oxygen can restart a stuck fermentation). Grape juice is exposed to air during normal crush operations and it becomes saturated with oxygen. Saturated juice at room temperature contains 5 milligrams of dissolved oxygen per liter, so yeast requires little additional oxygen to complete fermentation.

Oxygen Uptake

Oxygen always dissolves in wine stored in open containers or in closed containers having excessive headspace. The oxygen uptake on an **undisturbed** surface is about 20 milligrams per hour per square foot of exposed wine surface. Consequently, oxygen uptake depends largely on the surface area of wine exposed and the exposure time. Tall slender tanks are preferred to short, wide tanks because taller tanks have less exposed wine surface area.

Consider the situation of racking 750 gallons of wine from a 4-feet diameter tank into a similar tank. Racking is done with a transfer pump and the racking time is five hours. The exposed wine surface area is about 12 square feet, and two wine surfaces are involved (two tanks). Therefore, 480 milligrams of oxygen (20 X 12 X 2 = 480) will be dissolved in the wine each hour, and at the end of five hours, the wine will contain about 2400 mg of oxygen. There are 2850 liters in 750 gallons, so 2400 mg of oxygen divided by 2850 liters is 0.8 milligrams of oxygen per liter of wine. Since saturated wine holds about 7 milligrams of oxygen per liter, the wine in this example would be about 11 percent saturated with oxygen. Moving 750 gallons in five hours requires a pump capacity of 150 gallons per hour. Oxygen uptake is proportional to exposure time. So, more oxygen would be dissolved if a smaller capacity pump were used. Therefore, racking large tanks with small pumps should be avoided.

The above calculation shows how oxygen uptake can be estimated. However, calculating oxygen uptake this way can be misleading. Undisturbed wine surfaces were assumed, and smooth liquid surfaces are seldom the case. Considerable splashing and bubbling occur at the beginning of any wine transfer. Much turbulence is produced on the wine surfaces, and turbulence and bubbles can increase the exposed surface area by several hundred percent. Instead of 0.8 mg/l of oxygen uptake calculated above, 1 to 3 milligrams of oxygen per liter is commonplace even **when tanks are racked carefully**. Wine can be saturated with dissolved oxygen after racking when excessive splashing takes place or when an air leak occurs in the pump or in the suction line.

Bottle Head Space

Many small wineries use multi-spout, gravity fillers when bottling wine. Unfortunately, gravity fillers must be used carefully to avoid excessive oxygen uptake. Little bubbling occurs when bottles are filled slowly, but excessive amounts of foam can be generated when bottles are filled quickly. The foam exposes a very large surface area of wine to the air. Considerable oxygen dissolves into the wine, and the wine can become saturated with oxygen when bottles are filled carelessly. Saturated wine contains 7 milligrams of oxygen per liter, so a 750-ml bottle of wine contains 5.2 milligrams.

Some winemakers leave three or more inches of headspace (about 10 milliliters) in their bottled wines. Unless a vacuum corker is used, much of this air is compressed and remains in the bottle when the cork is driven. At room temperature, 10 milliliters of headspace contains about 2.8 milligrams of oxygen.

Scavenging oxygen is one of the more important reasons for adding sulfur dioxide to wine. But, deciding just how much sulfur dioxide should be in wine at bottling time is not easy because the bottling operation adds so much oxygen. Knowing four milligrams of sulfur dioxide are required to react with each milligram of oxygen can be used to estimate how much sulfur dioxide is needed at bottling time.

Consider this example. A wine containing little dissolved oxygen might become about 1/3 saturated with oxygen if the bottles are filled carefully. Each bottle of wine would then contain about 1.7 milligrams of dissolved oxygen. If the volume of the headspace is 5 milliliters, the headspace will contain about 1.4 milligrams of oxygen. So in this example, the newly bottled wine would contain 3.1 milligrams of oxygen. Four milligrams of sulfur dioxide are needed to react with one milligram of oxygen, so 12.4 milligrams of SO_2 would be needed to react with the oxygen in the bottle. A bottle contains 750 milliliters, so 16.4 milligrams of sulfur dioxide per liter of wine would be required to react with the oxygen. If the wine being bottled contained 30 milligrams of SO_2 per liter, a little more than half (12.4/30 = .55) of the SO_2 would be consumed by reacting with the dissolved oxygen, and about 14 milligrams of SO_2 per liter would remain in the wine to provide long term protection.

Here is a second example. Wine will probably be saturated with oxygen when bottles are filled carelessly and excessive splashing occurs. A 750-ml bottle of saturated wine contains about 5.2 milligrams of dissolved oxygen. Bottles under filled with wand-type fillers will have about 10 milliliters of headspace, and the headspace will contain 2.8 milligrams of oxygen. The total oxygen content in each bottle would be about 8 milligrams. Four milligrams of sulfur dioxide are required for each milligram of oxygen, so 32 milligrams of sulfur dioxide are needed to react with the dissolved oxygen in each bottle. Since a bottle contains 750 milliliters of wine, the wine being bottled would require about 43 milligrams of SO_2 per liter **just to react with the oxygen present**.

Removing Hydrogen Sulfide

Winemakers often splash wine vigorously to remove hydrogen sulfide gas. A disadvantage of this treatment is the possibility of oxidizing the wine, but wine oxidation can be reduced considerably if the splashing is done properly. Splashed wine quickly becomes saturated with oxygen. However, once saturated, no more oxygen can enter the wine, and the saturated wine can be splashed for an extended time to remove the hydrogen sulfide. Little more oxygen enters the wine, so little additional wine oxidation occurs. Here, one large exposure to air produces much less wine oxidation than if several small splashing treatments were applied over an extended time. Of course, considerable sulfur dioxide will be consumed when wine is handled in this way, so the free sulfur dioxide level of the wine should be measured and adjusted after any splashing treatment.

Barrel Aging

Dissolved oxygen slowly disappears as oxidation reactions occur in wine. Little air enters through the staves, so no significant oxidation takes place when wine is stored in tight barrels. However, additional air enters the barrel each time the bung is removed. Additional oxygen from the air then dissolves in the wine and begins a new oxidation cycle. This repeated process of exposing wine to small amounts of oxygen, followed by periods of almost no oxidation, contributes to wine quality. It is one of several desirable characteristics obtained from aging wine in barrels.

Oops

Novice winemakers often panic when they discover a bung lying on the floor because they are afraid the wine in the open barrel will be oxidized. Depending on storage conditions, wine in an open barrel can become saturated with oxygen quickly, but once saturated, little more oxygen enters the wine. Wine oxidation reactions occur slowly, so the wine in the open barrel remains saturated or nearly saturated for some time. Part of the dissolved oxygen reacts with sulfur dioxide and is slowly removed from the wine. Sulfur dioxide then continues to scavenge oxygen after the bung is returned to barrel. Consequently, a barrel of wine may be open for a day or so, but the saturation effect often prevents extensive wine damage. Of course, catastrophic oxidation damage will likely occur if the sulfur dioxide content of the wine is low or if the barrel remains open for several days.

Assessing Oxygen Uptake

Large wineries monitor the oxygen content of their wines with a dissolved oxygen meter, but a small winery often lacks this measurement capability. Fortunately, small producers can use simple SO_2 measurements to provide useful information about oxygen uptake. Recall that the molecular weight of sulfur dioxide is 64 and that of oxygen is 16. So, four milligrams of sulfur dioxide are required to react with one milligram of oxygen. Knowing the ratio of sulfur dioxide to oxygen allows winemakers to estimate oxygen uptake from routine free sulfur dioxide measurements.

One example above showed an oxygen uptake of about 2 milligrams per liter resulted from racking a 750-gallon tank of wine. Using the ratio of four to one, 8 mg/l of free SO_2 would be needed to combine with the 2 mg/l of dissolved oxygen. If the wine in the tank contained 20 milligrams of sulfur dioxide per liter before the transfer, about 12 mg/l of SO_2 would remain in the wine after the racking. The drop of 8 mg/l in sulfur dioxide could be detected by measuring the free SO_2 before and after racking.

Here is another example. Bottling always introduces considerable dissolved oxygen, and wine in newly filled bottles is often 1/3 saturated. Standard wine bottles are 3/4 liters, and saturated wine contains about 7 milligrams of oxygen per liter. Therefore, a bottle of 1/3 saturated wine contains 1.7 milligrams of dissolved oxygen. The volume of the headspace in bottles is about 5 milliliters, and room temperature air contains about 280 mg/l of oxygen per liter. So, the bottle headspace contains 1.4 milligrams of oxygen. Most of this oxygen will be driven into the bottle, so each bottle of corked wine would contain about of 3.1 milligrams of oxygen. Since 4 milligrams of SO_2 are required for each milligram of oxygen, 12.4 milligrams of SO_2 is needed to react with the dissolved oxygen in the bottle. Bottles hold three quarters of a liter, so 16 (12.4 / .75 = 16) milligrams of SO_2 per liter would be needed to react with the oxygen introduced during the bottling operation. If the wine contained 25 mg/l of free SO_2, about 9 mg/l of free sulfur dioxide would remain in the wine to provide continued protection.

Estimating oxygen uptake by measuring the decrease in free sulfur dioxide is not a very accurate method. The reaction between SO2 and oxygen requires some time. In fact, several days may be required for all of the dissolved oxygen to react with the sulfur dioxide. In addition, some dissolved oxygen always reacts with wine materials other than SO_2. Even so, useful estimates of oxygen uptake can be obtained by making accurate SO_2 measurements just before the wine is handled and then again several days after handling.

Summary

Much wine is spoiled by excessive oxidation each year. Oxygen diffuses into wine quickly, but depending on storage conditions, several days or even weeks may be required before all of the dissolved oxygen is consumed by chemical reactions. Wine saturated with oxygen contains about seven milligrams of oxygen per liter. When bottles are filled carelessly and when excess headspace is left, surprisingly large amounts of sulfur dioxide will be consumed (20 to 40 milligrams per liter). Useful estimates of oxygen uptake can be obtained from accurate SO_2 measurements.