

SULFUR DIOXIDE IN WINE

by
Lum Eisenman

In a reducing atmosphere, sulfur can be converted into hydrogen sulfide and other smelly compounds. Hydrogen sulfide smells like rotten eggs, and very small amounts can reduce wine quality. Other sulfur containing materials, such as mercaptan and disulfide also produce strong, undesirable odors. So even though all wines contain some sulfur, winemakers are always a bit apprehensive about sulfur compounds in their wines.

On the other hand, one sulfur compound can be very beneficial to the winemaking process, and most winemakers add small amounts of sulfur dioxide from the time the grapes are crushed until the wine is bottled. Some properties and some of the ways sulfur dioxide is used in winemaking are discussed below.

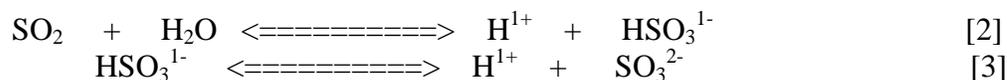
SULFUR CHEMISTRY

When elemental sulfur is burned, the sulfur combines with oxygen from the air and sulfur dioxide is produced. Chemists use a kind of "shorthand" notation to describe chemical reactions, and they might write an equation describing the production of sulfur dioxide as:



Here, the "S" represents an atom of sulfur, and the "(s)" indicates sulfur is a solid material. The "O" represents oxygen, the "sub 2" signifies two oxygen atoms and the "(g)" indicates that oxygen is a gas. The "=>" is a shorthand notation for "produces." The "SO₂" shows one molecule of a material called "sulfur dioxide" is formed, and the "(g)" indicates that sulfur dioxide is a gas. The above equation indicates that when sulfur burns, one atom of solid sulfur combines with 2 atoms of oxygen gas and a new gas called sulfur dioxide is produced.

When sulfur dioxide is added to wine, some of the gaseous SO₂ reacts with water in the wine and forms a hydrogen ion and a bisulfite ion. Then some of the bisulfite ionizes and produces a second hydrogen ion and a sulfite ion. These sulfur dioxide reactions with water can be written in the following way:



Equation [2] above shows that sulfur dioxide gas (SO₂) plus water (H₂O) produces a hydrogen ion (H¹⁺) and a bisulfite ion (HSO₃¹⁻). The "1+" following the H indicates that the hydrogen is ionized (it lost its only electron) and carries a positive electrical charge. The "1-" following the "HSO₃" shows the bisulfite is ionized (it gained an electron) and carries a negative electrical charge. Equation [3] above shows that bisulfite can ionize and produce a second hydrogen ion and a sulfite ion. Here, the "2-" following the "SO₃" shows the sulfite is doubly ionized (it gained two electrons) and carries two negative electrical charges.

One sulfur atom, three oxygen atoms and two hydrogen atoms are shown on each side of the double arrow symbol in equation [2]. In equation [3], one sulfur atom, three oxygen atoms and one hydrogen atom are shown on each side of the double arrow symbol. This is typical of chemical reactions. The equations show how the atoms rearrange, but note that **no materials are gained or lost**.

The arrowheads point in both directions in these equations, and chemists use double-headed arrow symbols when reactions can occur in either direction. Reading from left to right, equation [2] says...."Sulfur dioxide plus water produces a hydrogen ion plus a bisulfite ion." However, the equation can also be read from right to left. Then equation [2] says...."Bisulfite plus an ionized hydrogen atom produces water and sulfur dioxide."

The two equations above are often written as a single equation.



Equation [4] indicates that sulfur dioxide in water exists in three forms. (1) Some of the sulfur dioxide is not changed and exists simply as gas (SO₂) dissolved in water and this form is called **molecular** sulfur dioxide. (2) Some of the sulfur dioxide exists in the singly ionized **bisulfite** form (HSO₃¹⁻) and (3) some of the sulfur dioxide exists in the doubly ionized **sulfite** form (SO₃²⁻). The two double arrows in equation [4] also show how chemical equilibrium is maintained. For example, if a few SO₃²⁻ ions were to disappear for some reason, equation [4] shows that a spontaneous reaction would take place from left to right. A few HSO₃¹⁻ ions would be converted into SO₃²⁻ ions, and a few SO₂ molecules would be converted into HSO₃¹⁻ ions. The ratio of SO₂, HSO₃¹⁻ and SO₃²⁻ would then be restored and chemical equilibrium would be maintained.

Since the arrows point in both directions, this equation also shows the reaction can also take place from right to left. In this case, if some dissolved SO₂ disappeared for what ever reason, some of the HSO₃¹⁻ ions would spontaneously convert into SO₂ and some SO₃²⁻ ions would convert into HSO₃¹⁻ ions. The ratio of the SO₂, HSO₃¹⁻ and SO₃²⁻ would again be restored and equilibrium would be maintained.

BOUND SULFUR DIOXIDE

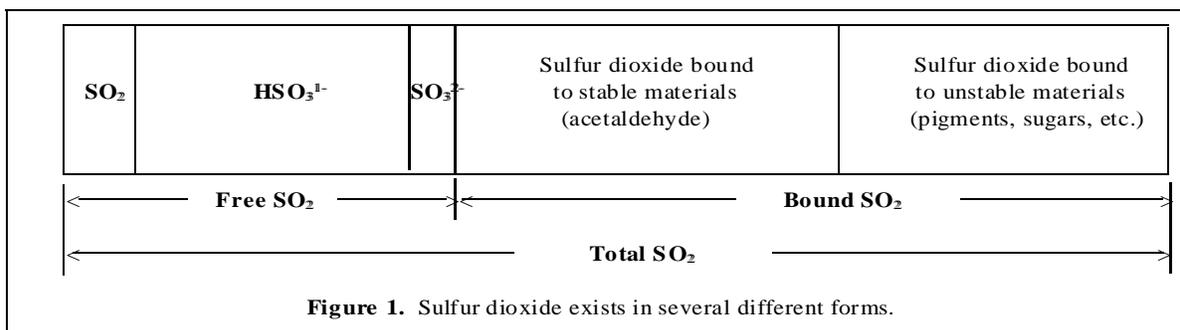
When sulfur dioxide is added to wine, part of the added sulfur dioxide combines with other wine materials, and part of the sulfur dioxide added to wine remains in the free form. The combined sulfur dioxide is chemically **bound** to these materials and no longer exists as free sulfur dioxide. The remainder of the added sulfur dioxide remains in a free state, and the **free** sulfur dioxide is the part that can ionize in water and behave as the equations above predict.

Wine materials that bind with sulfur dioxide fall into two general classes. Some materials such as acetaldehyde develop strong bonds with SO₂ and the bound sulfur dioxide becomes more or less permanently attached under normal wine conditions. Other wine materials, such as pigments, sugar, etc., bond rather weakly with SO₂. These bonds can be broken more easily and then some of the weakly bound sulfur dioxide can convert back into free sulfur dioxide.

When sulfur dioxide is added to young wines that contain small amounts of sulfur dioxide, about half the added sulfur dioxide quickly becomes bound and is no longer available as free sulfur dioxide. But, when sulfur dioxide is added to mature wines that contain relatively large amounts of sulfur dioxide, very little of the added sulfur dioxide becomes bound. For example, if 40 mg/l of sulfur dioxide is added to a new wine (containing little sulfur dioxide), about 20 milligrams of the added sulfur dioxide will become bound sulfur dioxide and about 20 milligrams of the added sulfur dioxide will remain in the free state. On the other hand, if 40 mg/l of sulfur dioxide is added to a mature win (containing considerable sulfur dioxide), then 30 to 35 mg/l of the added sulfur dioxide will remain in the free state. This spontaneous conversion of free SO₂ into bound SO₂ often confuses novice winemakers.

FREE SULFUR DIOXIDE

The relationship between molecular sulfur dioxide, bisulfite, and sulfite, and free, bound and total sulfur dioxide is shown below in Figure 1. Some of the sulfur dioxide is always bound to acetaldehyde, pigments, sugars, and other materials in the wine. The bound sulfur dioxide is more or less inactive so it is of little interest to the winemaker. The remaining sulfur dioxide in a wine is in the free state, and the free sulfur dioxide content of a wine is always of interest to the winemaker because free sulfur dioxide is the active form of sulfur dioxide.



Please note that the free SO_2 is divided into molecular sulfur dioxide, bisulfite (HSO_3^{1-}) and sulfite (SO_3^{2-}). The way free sulfur dioxide is divided between the three forms depends on wine pH. The distribution does not depend on the amount of free sulfur dioxide in the wine. For normal wine pH values (3.0 to 4.0), roughly 1/2 to 6 percent of the free sulfur dioxide exists in the molecular form, 94 to 99 percent of the free sulfur dioxide exists in the bisulfite form and only 0.01 to 0.12 percent exists in the sulfite form.

Table 1 shows how free sulfur dioxide is distributed as a function of wine pH. For example, if a wine has a pH of 3.1 and contains 12 mg/l of free sulfur dioxide, the wine would contain 0.59 mg/l of molecular SO_2 (0.049×12), 11.4 mg/l of bisulfite (0.951×12) and 0.0018 mg/l of sulfite (0.00015×12). Please note that the amount of molecular SO_2 strongly depends upon the pH of the wine and at high pH values, little of the free little SO_2 exists in the molecular form.

The free sulfur dioxide content of wine does not remain constant. Molecular SO_2 is a gas, some SO_2 gas escapes into the atmosphere each time a wine storage container is opened. Some bisulfate becomes bound with other wine materials slowly. Small amounts of sulfite are oxidized into sulfate (see below). So in general, the free sulfur dioxide content of wine slowly decreases. But, it can disappear from wine more rapidly in hot weather or when wine is handled (racked, filtered, bottled, etc.). Consequently, most commercial wineries measure the free SO_2 content of their wines every few weeks and additional sulfur dioxide is added as needed to maintain the molecular SO_2 level at about 0.8 milligrams per liter.

| Wine pH | % as Molecular | % as Bisulfite | % as Sulfite |
|---------|----------------|----------------|--------------|
| 3.0 | 6.1 | 93.9 | 0.012 |
| 3.1 | 4.9 | 95.1 | 0.015 |
| 3.2 | 3.9 | 96.1 | 0.019 |
| 3.3 | 3.1 | 96.8 | 0.024 |
| 3.4 | 2.5 | 97.5 | 0.030 |
| 3.5 | 2.0 | 98.0 | 0.038 |
| 3.6 | 1.6 | 98.4 | 0.048 |
| 3.7 | 1.3 | 98.7 | 0.061 |
| 3.8 | 1.0 | 98.9 | 0.077 |
| 3.9 | 0.8 | 99.1 | 0.097 |
| 4.0 | 0.6 | 99.2 | 0.122 |

Table 1. Wine pH determines how the free sulfur dioxide is distributed.

TOTAL SULFUR DIOXIDE

Winemakers use the term **total** sulfur dioxide when referring to the sum of both the free and bound sulfur dioxide in wine. Both total and free sulfur dioxide content can be easily measured, and the bound sulfur dioxide can be calculated from the measured values. Sulfur dioxide in the free form can react with oxygen and other materials in wine. But, sulfur dioxide in the bound state is no longer available to react with oxygen or other wine materials, so some winemakers feel bound and total sulfur dioxide is not very important. Even so, large amounts of total sulfur dioxide in a wine may indicate excessive microbial activity, excessive wine oxidation, poor storage conditions, etc. Federal regulations limit the total sulfur dioxide content of commercial wines, so wineries measure and track the total sulfur dioxide as well as the free SO₂ in their wines. Most home winemakers seldom bother measuring total sulfur dioxide unless a problem is encountered.

Molecular SO₂

Several scientific studies have shown the antiseptic properties of sulfur dioxide in wine depend on the form of the sulfur dioxide. Moreau and Vinet studied the antiseptic properties of sulfur dioxide and concluded that molecular sulfur dioxide was the effective form. Fornachon studied the characteristics of both fixed and free sulfur dioxide in Australian wines, and he showed several types of wine bacteria, including *Lactobacillus*, could be controlled by very small quantities of molecular sulfur dioxide. Other studies have also show that 0.5 to 1.2 milligrams of molecular sulfur dioxide per liter of wine can provide good microbial stability.

Today, most winemakers feel that 0.5 to 0.8 milligrams of molecular sulfur dioxide per liter of wine provides adequate protection for dry table wines. Consequently, most commercial wineries maintain at least 0.8 milligrams per liter of molecular sulfur dioxide in their white and blush table wines but only maintain 0.5 milligrams per liter of molecular sulfur dioxide in their high pH red table wines.

Most winemakers add an initial dose of 30 to 50 milligrams of sulfur dioxide per liter when grapes are crushed to help control native yeast. Contrary to much home winemaking literature, sulfur dioxide added at crush does not kill native yeast, but it does greatly diminish their activity for several hours. Commercial wine yeast has considerable tolerance to sulfur dioxide and remains active in the presence of normal amounts of sulfur dioxide. When commercial yeast is added to juice containing reasonable amounts of SO₂, a large population of the added yeast quickly develops while the native yeast is inactive. The commercial yeast then dominates the fermentation, and this is why all wine yeast manufacturers recommend adding yeast **immediately** after sulfur dioxide additions are made to juice or crushed grapes.

Since molecular sulfur dioxide is the effective antiseptic form, winemakers are always interested in how much molecular sulfur dioxide exists in their wines. The molecular form of sulfur dioxide is difficult to measure. However, free sulfur dioxide and wine pH can be measured easily. Then, the molecular sulfur dioxide can be obtained from the free sulfur dioxide and wine pH values.

| Wine pH | Free SO ₂ needed for 0.5 mg/l molecular SO ₂ | Free SO ₂ needed for 0.8 mg/l molecular SO ₂ |
|---------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| 3.0 | 8 (mg/l) | 13 (mg/l) |
| 3.1 | 10 | 16 |
| 3.2 | 13 | 21 |
| 3.3 | 16 | 26 |
| 3.4 | 20 | 32 |
| 3.5 | 25 | 40 |
| 3.6 | 31 | 50 |
| 3.7 | 39 | 63 |
| 3.8 | 49 | 79 |
| 3.9 | 62 | 99 |
| 4.0 | 78 | 125 |

Table 2. Wine pH determines the quantity of free SO₂ needed to produce 0.5 and 0.8 mg/l of molecular SO₂.

The amount of free sulfur dioxide needed to produce 0.5 and 0.8 milligrams of molecular SO₂ per liter for different values of wine pH is shown in Table 2. The table shows that acceptably small quantities of free sulfur dioxide can produce enough molecular sulfur dioxide to provide good microbial stability when wine pH is less than about 3.8. For example, the table shows that when wine has a pH of 3.4, then 32 mg/l of free sulfur dioxide produces 0.8 mg/l of molecular SO₂. Note that very large values of free SO₂ are required to produce 0.8 mg/l of molecular SO₂ when wine pH exceeds 3.8 or 3.9

The unpleasant “burnt match” odor sometimes detected in wine depends primarily on the amount of molecular sulfur dioxide present, rather than on the amount of free sulfur dioxide. Wine with a pH of 3.1 and containing 30 mg/l of free sulfur dioxide might have a noticeable sulfur smell due to the large amount of **molecular** sulfur dioxide. However, a wine with a pH of 4.0 and containing 120 mg/l of free sulfur dioxide might have little or no perceptible odor. (Even so, not many winemakers would bottle wines containing 120 mg/l of free sulfur dioxide).

Bisulfite

Most of the free sulfur dioxide in wine is in the bisulfite form. Bisulfite contributes little to the antiseptic or the antioxidant properties of sulfur dioxide, but bisulfite is of interest to winemakers. Alcohol is produced from sugar by a multi-step process. Several enzymes are involved, and the enzymes are produced by yeast. Acetaldehyde is produced in the next to last step of the fermentation process. Acetaldehyde is a volatile liquid and has a peculiar nut-like odor. Sherry wines contain relatively large amounts of acetaldehyde, and it is the acetaldehyde that gives sherry wines their distinctive nut-like odor.

Acetaldehyde is also produced when alcohol in wine oxidizes (acetaldehyde can be thought of as oxidized alcohol). Although desirable in sherry, this acetaldehyde odor is considered a fault in table wines. Excessive oxidation, with the accompanying sherry smell, is the most common fault found in homemade table wines. Bisulfite combines readily with acetaldehyde, and unless the wine is badly oxidized, much of the nut-like odor is eliminated. This is why small quantities of sulfur dioxide added to old, oxidized wines often makes the wine smell and taste fresher.

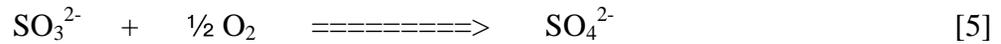
Bisulfite also bonds with phenols, pigments, sugars and other wine materials. However, the attachment between bisulfite and these other wine materials is relatively weak. These bonds can be easily broken, and then some of the bound bisulfite can then return to the free bisulfite form. Part of the weakly bound sulfur dioxide makes up a reservoir or pool, and this reservoir can supply some free sulfur dioxide back into the wine.

Normal levels of bisulfite only have a slight narcotic affect on yeast. However, some of the lactic bacteria are sensitive to bisulfite and more than about 50 mg/l of free sulfur dioxide can impede malolactic fermentation. Bisulfite has no smell, but excessive amounts of bisulfite may produce a "soapy" or "metallic" taste in wine.

Sulfite

At normal pH values, only a tiny fraction of the free sulfur dioxide is in the sulfite form. But, sulfite is important because it can deactivate enzymes and remove free oxygen from wine. Grape juice is in contact with the surrounding air during crush operations. The juice reacts with oxygen in the air and becomes oxidized. Oxidation causes the juice to turn brown, and browning is greatly accelerated by the presence of naturally occurring enzymes in the grapes. *Polyphenoloxidase* is the name of this enzyme, and it is the same enzyme that causes freshly cut apples to turn an unpleasant brown color. *Polyphenoloxidase* is sensitive to free sulfur dioxide in the sulfite form, so sulfite provides a tool for reducing enzymatic browning in both white and blush wines.

The sulfite form of free sulfur dioxide provides the anti-oxidant properties. Theoretically, sulfite can react directly with free oxygen in wine, but a two step process involving hydrogen peroxide removes most wine oxygen. In either case, sulfate (sulfuric acid) is produced and the oxygen in the wine is reduced.



This equation indicates thatsulfite reacts with oxygen ($\frac{1}{2} \text{O}_2$) and produces sulfate (SO_4^{2-}). But, the reaction is not quite so simple. First, oxygen in the wine reacts with a phenolic compound in the wine, and the oxygen is converted into hydrogen peroxide. Then, if free sulfur dioxide is present, the hydrogen peroxide reacts with sulfite. Sulfate and water are produced and oxygen has been removed from the wine.



The above equation shows how sulfite (SO_3^{2-}) reacts with hydrogen peroxide (H_2O_2) producing sulfate (SO_4^{2-}) and water (H_2O). The conversion of sulfite to sulfate is essentially nonreversible, so some free SO_2 is lost from wine when oxygen is removed.

Please note that equation 4 shows how protons are produced as sulfite disappears. When wine oxidizes in the presence of sulfur dioxide, the production of protons (as sulfite disappears) causes the pH of the wine to decrease and the titratable acidity to increase. This effect is small but it can be significant in high pH wines and a reduction of 0.1 or so in pH is often observed when high pH wines are aged in barrels for a year or more.

SUMMARY

Sulfur dioxide exists as both free sulfur dioxide and bound sulfur dioxide in wine. Free sulfur dioxide is the active form, and this is the form that protects wine against microbes, oxidation, etc. Bound sulfur dioxide is chemically bonded to other wine materials and this form plays a more or less passive role in winemaking. The sum of the free and bound sulfur dioxide is called total sulfur dioxide.

Free sulfur dioxide exists as molecular SO_2 , bisulfite and sulfite, and wine pH determines how free sulfur dioxide is distributed between these three forms.

Molecular SO_2 is the form effective against wine microbes, so winemakers try to maintain 0.8 mg/l of molecular SO_2 in their wines to foster bacterial stability. When wine pH is low, small amounts of free sulfur dioxide can be effective in controlling wine microbes. But, even excessive amounts of free sulfur dioxide may not produce enough molecular sulfur SO_2 to effectively control microbes in wines with high pH values. The unpleasant "burnt match" odor in wine is produced by the molecular sulfur dioxide content.

Bisulfite binds with acetaldehyde, pigments, sugars and several other materials in wine. Some of the oxidized odor is reduced when bisulfite binds with acetaldehyde. Some lactic bacteria are also sensitive to bisulfite, so large amounts of free sulfur dioxide can curtail malolactic fermentation. The bisulfite form has no odor.

The sulfite form of the free sulfur dioxide deactivates the enzymes in grape juice that cause browning. Sulfite also scavenges oxygen from wine. Sulfite has no odor.