



## WINE CHEM 101 PART C

### THE FINAL FRONTIER

By **BOB PEAK**

Last year in Part B of this ongoing chemistry lesson, I wrote about wine acids. As usual, I found it impossible to discuss acids without also mentioning pH—they are closely related. However, they do not measure exactly the same thing and must be determined separately if you want a full picture of your wine. While the titratable acid number—TA—is all about taste, the pH number is all about stability. **In particular, wine pH strongly influences the effectiveness of sulfite in preserving wine's freshness and quality. So a sulfite discussion follows this information on pH and wraps up the Wine Chem series.**

The range for pH is from 0 to 14. Water, representing neutral, is pH 7.0. Lower numbers (0-6.9) are acidic and higher numbers (7.1 to 14) are basic. The normal range for wine is about 3.0 to 4.0, occasionally going a little higher. pH is named that for good reasons—not just to drive non-chemists crazy! The lower-case “p” means “the negative logarithm of”. The capital H represents the hydrogen ion activity (concentration, more or less) of the acid solution. All of this is expressed in molar values—a mole of a substance is the gram equivalent of its molecular weight—but don't worry about that. It just puts all chemicals on an equal footing for reaction purposes.

Strong acids, like hydrochloric (muriatic) swimming pool acid, are essentially completely dissociated in water. That is, for every molecule of HCl that comes in contact with water, the H separates as a proton, H and the Cl separates as a chloride ion, Cl<sup>-</sup>. The gram equivalent weight of HCl is 36.5 grams. So, if we mix 3.65 grams (one tenth of a mole) in one liter of distilled water, the molar concentration is 0.1. Since all of the molecules dissociate for this strong acid, the hydrogen ion activity is also 0.1 molar. In scientific notation, we can express one-tenth as 10<sup>-1</sup>. Since the base-ten exponent of that number is -1, the logarithm of that number is also -1. That said, we look at the negative logarithm (p) by reversing the sign: 1. A one-tenth molar solution of hydrochloric acid has a theoretical pH of 1. In reality, we would get a measured value very close to that, because this strong acid is so fully dissociated in water.

Not so, however, for the weak acids of wine. Several factors influence pH. First, we have different carboxylic acids participating in the combined pH—primarily tartaric, malic, and lactic, but also possibly citric and succinic. In addition, the potassium salts of the weak acids participate, serving as reservoirs for acid ions as needed in the solution. The wine is “buffered”—it resists changing its pH—by all of these combinations. **So, settled in somewhere between pH 3 and pH 4, it is unlikely to change very much even if the acid level goes up or down significantly. That is why you cannot determine TA by measuring pH, nor the other way around.**

To measure pH in the home wine laboratory, the easiest technique is to use pH indicator “dip sticks”. Unfortunately, although easy, they are not usually accurate enough to make good winemaking decisions. Instead, winemakers seriously interested in measuring pH will use a pH meter as seen elsewhere in this catalog. Either a portable, hand-held meter or a bench meter is good enough for wine PH, but the portable meters may respond too slowly to be useful for TA measurement if you want to get double-duty out of your meter. Many years ago, a very skilled Aus-trian chemist named **Martha Steinmetz** told me, **“everything is pH dependent.”** She said it often, and it is usually true. As noted above, our next chemistry topic is sulfur dioxide, and its behavior in wine is very pH dependent, indeed.

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**Sulfur dioxide, SO<sub>2</sub>, is a gas. When dissolved in water, it has a very vigorous reaction, producing dissolved sulfurous acid:**

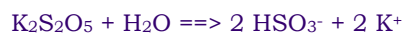


As it proceeds through the reaction, two protons are involved, just as with the dicarboxylic acids discussed in last year's article (although this is a simple mineral acid, it just happens to have two active protons). The pKa's (acid dissociation constants) are 1.77 and 7.22, shown as the (K1) and (K2) reactions above. These indicate that half of the "first" protons are dissociated at pH 1.77 and half of the "second" protons at pH 7.22. Since our wine has a pH between 3 and 4, only (K1) plays a significant role, and the dominant form of sulfur dioxide at wine pH is the bisulfite ion, HSO<sub>3</sub><sup>-</sup>. **However, it is sulfur dioxide in its molecular form, SO<sub>2</sub>, that is strongly antiseptic and antioxidant—protecting your wine from spoilage.**

Reactive, available sulfur dioxide measured in wine is called "free SO<sub>2</sub>" or "free sulfite". (Note, by the way, that "-ite" ending on sulfite. Sulfate, with an "-ate" ending is a completely different ion and plays no role in protecting your wine.) As we have seen from the pH discussion, most of the free sulfite is actually in the form of the bisulfite ion. Bi- in this case means "one hydrogen atom and one something else" rather than the more common meaning of "two". Potassium bisulfite, for instance, would be KHSO<sub>3</sub>.

**So, how free is it?** The amount of molecular SO<sub>2</sub> available to protect your wine depends on both the concentration of free sulfite and the pH of the wine. Red wines are generally considered to need 0.5 ppm of molecular SO<sub>2</sub> for protection from oxidation and spoilage, with white wines needing more, about 0.8 ppm. [On page 11 of this newsletter you will find a table that displays the needed free sulfite level to achieve effective molecular levels at various wine pH's.] And now you know one of the main reasons why low pH wines are more stable than high pH wines!

So far, this discussion has presented sulfite addition as though it came directly from added sulfur dioxide gas. Wineries do that, but sulfur dioxide is a dangerous and reactive chemical not appropriate for home winemaking. Instead, we usually add potassium metabisulfite, a potassium salt of sulfur dioxide. In this application, "meta" is a chemical term meaning "about to become." As above, the "bi" denotes that there is the one proton we have already discussed, plus one potassium ion. Consequently, when potassium metabisulfite is dissolved in water, our old friend the bisulfite ion is produced:



But, even though this presentation looks as though everything goes to bisulfite, we are still pH dependent. Once the bisulfite ion is in the wine, it can begin going back and forth to the other forms, including molecular sulfur dioxide.

### **So, how do all these "sulfite" terms add up?**

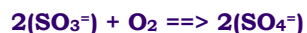
Potassium metabisulfite weighs 222.32 grams per mole. Sulfur dioxide gas weighs 64.1 grams per mole. For every mole of the salt you dissolve in water (or wine), the yield as sulfur dioxide is as if you added two moles of the gas. As a result, 222.32 grams of potassium metabisulfite introduces the same amount of activity as would 128.2 grams of sulfur dioxide gas (potassium, harmless to the wine, makes up the missing mass). That means that for every 100 ppm of potassium metabisulfite we use in our wine, we have added the equivalent of 57.7 ppm of sulfur dioxide. So, view 100 ppm as "total potassium metabisulfite added." **Does that mean "total SO<sub>2</sub>" is 57.7 ppm? No. The term "total SO<sub>2</sub>" is operation-ally determined in wine testing laboratories.** That is, instead of "total", it means something like "total sulfur dioxide that is recoverable by the recognized analytical method." In that method, a



chemist adds strong acid to a wine sample to force the sulfite back over into molecular sulfur dioxide. As that reaction proceeds in a heated flask, air is swept through the sample, removing the sulfur dioxide gas as it forms. At the other end of some glass apparatus, the gas is caught in a basic trapping solution. The chemist measures the amount caught, and that is called “total sulfite.” Not surprisingly, in our case, the

number would be somewhat less than the theoretical number of 57.7 ppm. From whatever that lower amount is, a still lower amount will be “free”—available to react. And only “free” produces molecular (which protects wine) as noted above. **See Page 10 in this catalog for more information on testing for free SO<sub>2</sub>.**

So, home winemakers always ask, “where did it go?” We have the tiny amount of molecular sulfur dioxide in the wine. We also hope to have a substantial amount of “free” sulfite—maybe up around 30 ppm. Most of that is in the form of the bisulfite ion. In the “total” measured by the appropriate test, we have all of the “free” included, plus some unstable reaction products that loosely link sulfite with other molecules such as sugars and some trace acids. Some of these may return to the “free” side of the ledger as other free sulfite is used up, serving as a sort of reservoir of free sulfite. Other links are not going to come apart, leaving that part of the “total” sulfite bound and unavailable. Those stable sulfite-containing compounds are mostly sulfited aldehydes—oxidation products in the wine that have been safely taken care of by the sulfite, but took the sulfite away with them. So although this sulfite is not coming back, neither are the aldehydes, and that is a good thing. But, as noted earlier, some “added” sulfite is not even in the “total.” Those sulfites are gone forever, mostly oxidized to sulfate (it’s that -ite and -ate thing again). Sulfate is very common in wine and in the environment, is non-reactive, and is non-toxic. It is what becomes of sulfur dioxide as the wine is exposed to air:



Since that sulfite is gone forever, it helps explain why you keep that barrel topped up and oxygen out!

**But what about “safe” SO<sub>2</sub> levels?** The legal maximum for total SO<sub>2</sub> in wine is around 350 ppm (and remember, the amount added can be higher still, without hitting the “total” limit, because some of it disappears). Dried fruit is allowed to contain up to 2,000 ppm. When people are adversely affected by sulfites, it is usually reflected as respiratory problems in sensitive individuals, often asthmatics. As I looked for a good illustration for this article, I came across an interesting case study. It seems that an alert emergency room physician noticed that he had six patients who had all consumed the same brand of salsa. Two of the patients had asthma flare-ups, two experienced coughing and tightness of the throat, and two required mechanical ventilation. It was discovered that the offending salsa had a sulfite content of 1,800 ppm—well above the level of 700 ppm found in other brands of salsa. One of the patients, fully aware of her sulfite sensitivity, thought it was safe to eat the salsa because it was improperly labeled as “fresh.” (Nagy, S. M., S. S. Teuber, S. M. Loscutoff and P.J. Murphy, J. Food Prot. (58) pp. 95-97. 1995).

**So what does it all mean?** Well, don’t add 700, 1,000, or 1,800 ppm of sulfite to your wine. Just don’t go there. Keep it to 30 ppm or so, added frequently and measured often. If problems do develop from sulfite in wine, they will likely be respiratory, particularly in sensitive individuals. If one of your friends says they cannot drink your wine because it gives them a headache, it isn’t the sulfites. They’re drinking too much wine!



This article concludes our three-year series of Wine Chem 101. We have covered sugar, alcohol, acids, pH and sulfites. **If you keep all of it in mind as you make this year's wine, you can envision your ideal wine chemistry: enough sugar to yield a desirable alcohol level; acids in the right range to be pleasant, refreshing, and balanced; pH where it can safely protect the wine from spoilage, and enough sulfur dioxide to get it safely into the bottle.** Chemistry is where science meets art in making fine wine!