Understanding molecular SO_2 calculators

A previous Ask the AWRI column (January, 2017) described the importance of molecular SO_2 and how to calculate it. This column responds to recent questions received by the AWRI helpdesk about the different online molecular SO_2 calculators available and why they can give different results.

Sulfur dioxide is converted to three different forms when added to wine.

What are the different forms of SO_2?

Sulfur dioxide (SO_2) exists as a gas but when added to wine it converts to three different forms: molecular (SO_2), bisulfite (HSO_3-) and sulfite (SO_3^{2}-). All three forms exist in wine in an equilibrium, as shown in Figure 1.

The amount of each form of SO_2 in a juice or wine is dependent on the wine pH. Ka_1 and Ka_2 are 'dissociation constants' and represent the pH values at which the two forms of SO_2 involved in the equilibria exist in equal amounts. For the pH range 3.0 to 4.0 (shaded in purple), the molecular SO_2 (mSO_2) declines from ~8% to 1% and the bisulfite ion increases from 92 to 99%. As only 0.02 to 0.04% of the SO_2 exists in the sulfite (SO_3^{2-}) form at wine pH, the mSO_2 calculation is based solely on the first equilibrium ($SO_2 \rightleftharpoons HSO_3^-$), so only the Ka_1 value is used.

Why do I get different values for mSO_2 depending on the website/calculator that I use?

The relationship between molecular and free SO_2 is given by the equation:

Molecular SO_2 = free SO_2 / $(1 + 10^{pH-pKa1})$, where $pKa_1 = -\log_{10}Ka_1$

This means that if the free SO_2, the pH and Ka_1 are known, mSO_2 can be calculated. The differences observed for mSO_2 values from different calculators is due to the use of different values for Ka_1 (and hence pKa_1) in the formula.

What's the importance of pKa_1 and why are different values used?

Apart from pH, several other wine parameters influence the amount of SO_2 in the molecular form. Temperature, alcoholic strength and ionic strength (a measure of the concentration of all the ions in solution) all affect the value of pKa_1 and consequently the level of mSO_2. The effects of these parameters on mSO_2 are summarised in Table 1.

As ionic strength is not something most wineries can easily determine, a value of 0.038M is commonly used in online calculators. This value is the approximate midpoint of the ionic strength range of 0.016 to 0.056M reported for wines (Delfini and Formica 2001).

The effect of temperature and alcohol on the concentration of mSO_2 are much greater than that of ionic strength. Using the ionic strength value above (or similar value), some online

calculators allow users to input alcohol and temperature measurements. Such calculators may provide a more accurate estimation of the mSO_2.

The AWRI's mSO_2 calculator (available on the AWRI winemaking calculators webpage and app) uses a value of 1.81 for the value of pKa_1, which is the value for SO_2 in water at 25°C. The use of this value is somewhat historical in that it's the value that was used by early wine authors to calculate levels of mSO_2 recommended to control microorganisms in wine. For example, Beech et al. (1979) used this value to calculate the mSO_2 concentration range (0.54 to 0.9 mg/L) recommended to restrict the growth of Saccharomyces cerevisiae yeast. This same value for pKa_1 was used by AWRI researchers when recommending mSO_2 concentrations above 0.625 mg/L to inhibit the growth of Brettanomyces in red wines (Curtin et al. 2012). Given the same pKa_1 value has been used by the AWRI to calculate mSO_2 for many years, current mSO_2 values obtained using the AWRI's calculator can be directly related to historical values. This can be useful, for example, if a winemaker found that a level of mSO_2 for a particular wine style was insufficient in the past and therefore needed to be increased. Such comparisons with historical values would not possible if the AWRI updated its calculator to consider variations in alcoholic strength and temperature.

> **Apart from pH, several other wine parameters influence the amount of SO_2 in the molecular form**

Molecular SO_2 calculators that incorporate alcoholic strength and temperature are likely to return higher values for mSO_2 than the AWRI calculator, which is likely to give an underestimation of the 'true' level of mSO_2. It should also be noted that SO_2 is typically measured at around 20–22°C, so mSO_2 values calculated based on a free SO_2 result in this temperature range will be an overestimation of the true concentration of mSO_2 if the bulk wine is actually stored at a lower temperature.

For further information on molecular SO_2 or any other grapegrowing and winemaking technical matters, contact the AWRI helpdesk on helpdesk@awri.com.au or 08 8313 6600.

Table 1. Effect of increasing temperature, alcoholic strength and ionic strength on pKa_1 and the concentration of mSO_2

Parameter	Effect on pKa_1	Effect on mSO_2 concentration
↑ Temperature	↑	↑
↑ Alcoholic strength	↑	↑
↑ Ionic strength	↓	↓

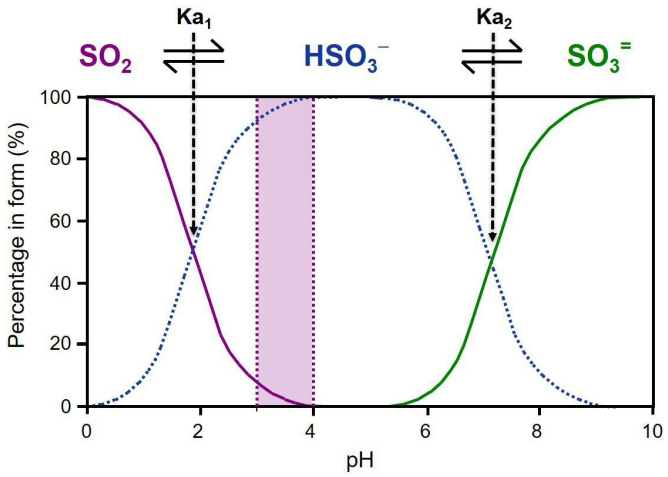

Figure 1. Different forms of sulfur dioxide (SO_2) as a function of pH in dilute solution

References

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