Wine Acid-base Chemistry

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September 2003

Contents

1 The Problem

We have elsewhere discussed the reason for the creation of this Java applet, and the associated documentation. Here we explore the mathematical basis for the applet, and some implementation details.

2 A little maths

Consider a kilogram of wine, with certain ‘known’ values (independent variables):

1. The initial and final pH;[1]
2. The titratable acidity, TA of the wine, espressed as grams/kg of tartaric acid;
3. Assumed initial ratios of each of the five acids (malic, citric, succinic, lactic and acetic acid), to tartaric acid;
4. The equilibrium constants at 25 ^{o}C for the various equations of dissociation of the acids.

From the above, we wish to determine ‘unknowns’, including the concentrations of the various acids, and the concentrations of their various ionic species.

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[1] Here, these are knowns, and not to be determined, as was the case in our exploration of the Stewart approach to acid-base in human plasma.

2.1 Conventions

Here's our list of notational conventions. Some of them are a little arbitrary, but they work for us!

1. We will abbreviate the six acids listed above as 'tar' and 'mal, cit, suc, lac, ace'.We will refer to an acid as A_x, x={tar, mal, cit, suc, lac, ace}, or $x = 0 \ldots 5$, and the concentration of a particular ionic species of such an acid as $[A_x^{-i}]$, where i is the ionisation state of the acid, $i = 0 \ldots \max(x)$, and $\max(x)$ in turn is the maximum ionisation state of the acid x.[2]
2. We will abbreviate the total concentration of a particular acid to $[A_x^{\mathrm{tot}}]$.
3. We will represent the dissociation constants of the acids as K_x^i, where x refers to the relevant acid and i is the ionisation state in the equation:[3]

$$A_x^{-i} \rightleftharpoons H^+ + A_x^{-(i+1)}$$

4. We will call the ratio of the molal concentration of a particular acid x to the molal concentration of tartaric acid 'C_x'.

2.2 Assumptions

We will use the following simplistic assumptions:

1. We will ignore the effects of the alcohol present on the permittivity of the solution, and on the activity coefficient of hydrogen ions and other ions;
2. We will conveniently (and very simplistically) ignore the 'common ion effect' and the non-unity activity coefficients of the various species of ion;
3. We will assume that at no stage is the solubility coefficient of any pair of ionic species exceeded, causing precipitation of e.g. potassium bitartrate!
4. We will assume that commonly available values for the various dissociation constants are accurate, apply at 25 ^{o}C, and make no comment about whether their determination involved correction for activity coefficients, etc.

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[2] Note that $[A_x^0]$ is the concentration of unionised acid in solution.

[3] Note that K_x^0 will be our rather peculiar representation of the more usual dissociation constant K_1 for that acid.

5. Finally, we assume that the PCO_2 of the wine is negligible (Clearly an inappropriate assumption for sparkling wines)!

2.3 Solving for the unknowns

Our general approach will be:

1. Convert the TA (as grams of tartaric acid per kg of wine) to a molal amount of 'acid titration' — we will refer to this amount as $[M]$.

2. Note that:

$$[M] = [H^+] + \sum_{x=0}^{5} \left(\sum_{i=0}^{\max(x)-1} (\max(x) - i).[A_x^{i-}] \right) \tag{1}$$

   This equation is a little tricky. We wish to titrate in a strong base (NaOH) until all acid species have been neutralised. Once titrated, 'all' of the currently undissociated or partially dissociated organic acid molecules in solution will be maximally negatively charged and have corresponding sodium ion(s) to balance this charge. There is a catch: some of the current negative charges are counter-balanced by hydrogen ions, which will almost completely disappear after full titration, to be replaced by sodium ions. So we add in the concentration of hydrogen ion!

   An alternative way of expressing [M] is:

$$[M] \approx \sum_{x=0}^{5} \max(x)[A_x^{\mathrm{tot}}] - \mathrm{SID} \tag{2}$$

3. We know that, for any equilibrium:

$$K_x^i = \frac{[H^+].[A_x^{-(i+1)}]}{[A_x^{-i}]} \tag{3}$$

   We can therefore express $[A_x^i]$ for $i > 0$, in terms of $[A_x^0]$, $[H^+]$ and K_x^i.

4. For each acid, by definition,

$$[A_x^{\mathrm{tot}}] = \sum_{i=0}^{\max(x)} [A_x^{-i}] \tag{4}$$

   This simply says that the total amount of the acid per kilogram of wine is the sum of the molal concentrations of the various ionic species (including the concentration of unionised acid).

5. For each acid, again by definition:

$$[A_x^{\text{tot}}] = C_x.[A_{\text{tar}}^{\text{tot}}] \tag{5}$$

We use the above equations to calculate our unknowns. From (3) we can express the concentration of any $A_x^{-i}, i > 0$ in terms of $[H^+]$, K_x^i and A_x^0. Similarly, we can use (4) to express any ionic species in terms of $[A_x^{\text{tot}}]$ and various knowns. We can then in turn use (5) to express any ionic species in terms of knowns, and $[A_{\text{tar}}^{\text{tot}}]$. Finally, we substitute for the various ionic species in (1), replacing each species in turn by a value expressed as a function of various K, C, $[H^+]$ and $[A_{\text{tar}}^{\text{tot}}]$. We now have a single equation with just one unknown, $[A_{\text{tar}}^{\text{tot}}]$, so we can calculate this last value, and use it to calculate the concentration of all other species.

2.4 Adding acids

We next consider the case where the desired pH is lower than the initial pH. We achieve this new pH by adding either tartaric acid, malic acid, or both. From the above calculations, we know the initial concentrations of each acid, $[A_x^{\text{tot}}]$. We also know the desired, final pH, so all we need to calculate is:

1. The amount of tartaric acid that we would need to add to achieve the desired pH, without addition of any other acid. Let's call the increase in molal concentration corresponding to this amount $[Q_{\text{tar}}^{100}]$.
2. The amount of malic acid required to achieve the same pH, on its own;
3. For each amount of tartaric acid added, in steps of, say, 1% from no added tartaric acid up to $[Q_{\text{tar}}^{100}]$, how much malic acid we would have to add!

2.4.1 Only adding tartaric acid

We will adopt the convention that new, unknown concentrations (after the addition of acids, with a corresponding change in pH) are referred to with a prime symbol, thus: $[A_x]'$. In the first instance, how do we calculate $[Q_{\text{tar}}^{100}]$? Well, we know that our new total concentration of tartaric acid, $[A_{\text{tar}}^{\text{tot}}]'$ is the sum of the old concentration and $[Q_{\text{tar}}^{100}]$:[4]

$$[A_{\text{tar}}^{\text{tot}}]' = [A_{\text{tar}}^{\text{tot}}] + [Q_{\text{tar}}^{100}] \tag{6}$$

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[4] Well, technically not entirely correct, as we have changed the total mass of the solution by adding mass, but the alteration is fairly small, and we will simplistically neglect it!

We can use (3) to express any of the new concentrations of tartaric acid species in terms of the various constants, and $[A^0_{\mathrm{tar}}]'$. We can then use (4) to express $[A^0_{\mathrm{tar}}]'$ in terms of $[A^{\mathrm{tot}}_{\mathrm{tar}}]'$.

We also know from considerations of charge balance, that

$$[H^+] + [\mathrm{SID}] = \sum_{x=0}^{5} \left(\sum_{i=1}^{\max(x)} i.[A_x^{i-}] \right) + [OH^-] \tag{7}$$

In other words, the sums of the concentrations of positive ions equals that of the concentrations of negative ions multiplied by the charges of each of these ion species. [SID] is of course the Strong Ion Difference, and in the case of wine will be predominantly made up of calcium and potassium ions. At a pH about 4, we can neglect $[OH^-]$.

The SID will not change, with the added tartaric acid, and the concentrations of all of the ionic species apart from tartaric acid can be calculated, as we know the total amounts of these acids, and, knowing the pH, can work out the concentrations of the other species. All we don't know in the above equation is the new concentrations of the various species of tartaric acid. We can express these in terms of $[A^{\mathrm{tot}}_{\mathrm{tar}}]'$, as above.

We now can calculate $[A^{\mathrm{tot}}_{\mathrm{tar}}]'$, and thence derive all unknowns.

2.4.2 Only adding malic acid

We can use an analogous argument to calculate the amount of malic acid required. Determine concentrations of all of the ionic species for the new pH, express all the malic species in terms of $[A^{\mathrm{tot}}_{\mathrm{mal}}]'$, substitute into (7), and we're away!

2.4.3 Combinations of malic and tartaric acid

We will consider various concentrations of tartaric between 'no added tartaric acid' and $[Q^{100}_{\mathrm{tar}}]$. We will refer to these as $[Q^1_{\mathrm{tar}}] \ldots [Q^{99}_{\mathrm{tar}}]$, the idea being that we will increase the amount of tartaric in 1% increments, and then calculate the required amount of malic acid. This calculation will be relatively straightforward, as we have already calculated $[Q^{100}_{\mathrm{tar}}]$. We can now vary the amount of tartaric acid added, as a percentage of $[Q^{100}_{\mathrm{tar}}]$, and calculate the various ionic species for all acids apart from malic acid. We can then substitute these into (7), and use the above logic (Section 2.4.2) to calculate the amount of malic acid required.

2.5 ML fermentation

Here, we will stochiometrically convert malic acid to lactic acid, to try and raise the pH to a target level. There are three possibilities:

1. Complete ML fermentation will be insufficient to achieve the desired pH change;
2. Complete ML fermentation is not required, as partial fermentation will be sufficient to raise the pH to the desired point;
3. Rarely, complete ML fermentation will achieve precisely the desired pH.

We will put ML fermentation and addition of base (potassium carbonate) onto the same convenient graph, plotting amount of K_2CO_3 added against amount of ML fermentation, up to the maximum amount of ML fermentation required to achieve the desired pH.

2.6 Adding base

Here we have a well-defined question — "How much base do we have to add to raise the pH by a certain amount?" What we are effectively doing by adding a base (be it sodium hydroxide or potassium carbonate) is adding positive ions, and thus increasing the strong ion difference.

Rather than simply providing a single number, we will perform the whole titration up to a pH of ~ 8.2.[5]

We will provide a graph of 'amount of added NaOH' against pH. The calculation will involve progressively altering the SID from the initial value we calculate, and then determining pH for every alteration.

In a manner similar to our initial Stewart work, we can take (7) and substitute in various values for the SID. We then solve for pH, and we're away!

3 Algorithms

In this section we will create detailed algorithms for our acid-base calculator.

From the above, we can see that we require three algorithms, related to adding malic and/or tartaric acid to achieve a lower pH, ML fermentation,

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[5] This might provide a 'reality check' of our equations and solutions, as any winemaker can simply titrate a wine sample with NaOH, measure the pH change as the base is titrated in, and check the titration graph against ours, possibly revealing the deficiencies in our model!

and titration against base. We will consider each in turn, but note that for each, there is a common initial algorithm, and that this in turn depends on several other algorithms. Here goes!

3.1 Common initial algorithm

1. Initialise all constant values — the various K_x^i, as well as an array of $\max(x)$ for the six acids.
2. Read in the initial pH, the initial TA, and the (molal) ratios of the acids with respect to tartaric acid, i.e. an array of five values of C_x.
3. Calculate $[M]$, as described in Section 3.2.
4. Calculate the values of $[A_x^{\text{tot}}]$ for each acid, using the algorithm below (Section 3.3).
5. Calculate the SID, as below (Section 3.4).

3.2 Find $[M]$

How exactly is TA determined by wine-makers? They add NaOH, and then express the added amount in terms of tartaric acid (g/kg),[6] as if they were adding it to pure tartaric acid solution!

The conversion is straightforward, once you realise that for every mmol of added tartaric acid, once titration has been completed, there will be two mmol of sodium ion, forming bisodium tartrate. The molal quantity of tartaric acid is simply the number of mols of sodium hydroxide added, divided by two.[7]

So, to 'reverse engineer' the amount of NaOH added, simply divide the TA by the molecular weight of tartaric acid (150.09) and multiply by two.

A false argument would be to try and calculate [M] as:

$$[M] = 2.[A^0_{\text{tar}}]^* + [A^-_{\text{tar}}]^*$$

…as this incorrect equation fails to take into account the substantial number of hydrogen ions which are paired with A^{2-} and A^- ions, and will disappear at higher pH, to be replaced by sodium ions!

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[6] Or is it g/l, in which case we must convert?

[7] Hmm. look at the small matter of added volume/mass, esp at 25^{o}C.

3.3 $[A_x^{\mathrm{tot}}]$ Calculation

1. For each acid x, express $[A_x^-]$ in terms of K_x^0, $[H^+]$ and $[A_x^0]$, using (3). In other words:

$$[A_x^-] = \frac{K_x^0 [A_x^0]}{[H^+]}$$

2. Where appropriate, repeat this process for $[A_x^{2-}]$, and so on:

$$[A_x^{2-}] = \frac{K_x^1 [A_x^{1-}]}{[H^+]}$$

$$[A_x^{3-}] = \frac{K_x^2 [A_x^{2-}]}{[H^+]}$$

3. We now have concentrations of each ionic species of A_x in terms of $[A_x^0]$;
4. Use (4) to relate $[A_x^{\mathrm{tot}}]$ and $[H^+]$, the various K_x^i, and $[A_x^0]$:

$$[A_x^0] = \frac{[A_x^{\mathrm{tot}}]}{1 + \frac{K_x^0}{[H^+]}\left(1 + \frac{K_x^1}{[H^+]}(1 + \frac{K_x^2}{[H^+]})\right)}$$

$$[A_x^{1-}] = \frac{[A_x^{\mathrm{tot}}]}{\frac{[H^+]}{K_x^0} + 1 + \frac{K_x^1}{[H^+]}(1 + \frac{K_x^2}{[H^+]})}$$

$$[A_x^{2-}] = \frac{[A_x^{\mathrm{tot}}]}{\frac{[H^+]}{K_x^1}\left(\frac{[H^+]}{K_x^0} + 1\right) + 1 + \frac{K_x^2}{[H^+]}}$$

$$[A_x^{3-}] = \frac{[A_x^{\mathrm{tot}}]}{\frac{[H^+]}{K_x^2}\left(\frac{[H^+]}{K_x^1}\left(\frac{[H^+]}{K_x^0} + 1\right) + 1\right) + 1}$$

5. Use (5) and the above to express each species of each acid in terms of $[A_{\mathrm{tar}}^{\mathrm{tot}}]$.

$$[A_x^0] = \frac{C_x . [A_{\mathrm{tar}}^{\mathrm{tot}}]}{\left(1 + \frac{K_x^0}{[H^+]}\left(1 + \frac{K_x^1}{[H^+]}(1 + \frac{K_x^2}{[H^+]})\right)\right)} \tag{8}$$

…and so on!

Let us abbreviate the above to:

$$[A_x^{i-}] = \frac{C_x.[A_{\text{tar}}^{\text{tot}}]}{\theta_x^{i-}} \tag{9}$$

Note that θ is a *function* of $[H^+]$, and that we say θ_x^{i-} rather than $\theta([H^+], i, x)$ for reasons of clarity.

6. Substitute the values from the preceding step into (1) to relate $[M]$ and $[A_{\text{tar}}^{\text{tot}}]$. We can calculate $[A_{\text{tar}}^{\text{tot}}]$, knowing that:

$$[M] = [H^+] + [A_{\text{tar}}^{\text{tot}}]. \sum_{x=0}^{5} C_x. \left(\sum_{i=0}^{\max(x)-1} \frac{\text{max(x)} - i}{\theta_x^{i-}} \right) \tag{10}$$

7. Use the value of $[A_{\text{tar}}^{\text{tot}}]$ thus derived to calculate each $[A_x^{\text{tot}}]$.

3.4 SID calculation

1. Use the values from above (Section 3.3) and (3) to determine the concentrations of each ionic species;
2. Substitute these, and $[H^+]$, into (7), to determine SID.

3.5 Adding acid

1. Read in the desired pH.
2. Calculate $[Q_{\text{tar}}^{100}]$ needed to achieve this pH, as explained below in section 3.6. Store this value.
3. For 1% increments from zero to $[Q_{\text{tar}}^{100}]$, calculate the amount of malic acid that must be added. Do so by introducing a percentage of $[Q_{\text{tar}}^{100}]$ calculated above, and using a procedure analogous to section 3.6, but with $[A_{\text{mal}}^{\text{tot}}]'$ as the unknown. Store the values of malic acid required to be added in a 100 element array.

3.6 Calculating $[Q_{\text{tar}}^{100}]$

1. For the new pH, calculate $[H^+]$.
2. For each acid x, apart from tartaric, use our knowledge of $[A_x^{\text{tot}}]$ and the equations from Section 3.3 to determine the concentrations of each ionic species at the new pH.

3. Substitute the values for the various concentrations of acid species into (7). Note that from this equation we derive:

$$[H^+] + [\text{SID}] = \sum_{x=1}^{5}\left(\sum_{i=1}^{\max(x)} i.[A_x^{i-}]\right) + \sum_{i=1}^{2} i.[A_0^{i-}]$$

   or, substituting (9) into the above:

$$[H^+] + [\text{SID}] = \sum_{x=1}^{5}\left(\sum_{i=1}^{\max(x)} i.[A_x^{i-}]\right) + C_0.[A_{\text{tar}}^{\text{tot}}]' \sum_{i=1}^{2} \frac{i}{\theta_0^{i-}}$$

4. Solve for $[A_{\text{tar}}^{\text{tot}}]'$:

$$[A_{\text{tar}}^{\text{tot}}]' = \frac{[H^+] + [\text{SID}] - \sum_{x=1}^{5}\left(\sum_{i=1}^{\max(x)} i.[A_x^{i-}]\right)}{\sum_{i=1}^{2} \frac{i}{\theta_0^{i-}}} \tag{11}$$

3.7 Calculating added malic acid

We know the total amount of tartaric acid required to lower the pH to the desired value. We can divide the amount we need to add into, say, 100 convenient fractions, and then, for each fraction, calculate the corresponding amount of malic acid, thus:

1. For 'Q^1' (Add just 1% of the total amount of tartaric acid), determine concentrations of the various species of tartaric acid *at the desired pH.*
2. In a manner analogous to the above, determine the amount of malic acid we need to achieve the desired final pH. Store this amount of malic acid in an array;
3. Repeat for all other fractions of tartaric acid.

3.8 ML fermentation

1. For a conversion of (say) 1% of the malic acid into lactic acid, recalculate the concentrations of all acid species *at the target pH.* Substitute all of these values into (7) to determine the *new* SID. The difference between the former SID and the new SID represents the molal quantity of positive (potassium) ions we still need to add to raise the pH after the given quantity of ML fermentation has been achieved. If the value is zero, we need add no more K_2CO_3, and if negative, then ML fermentation has more than achieved our pH goal!

2. Repeat the calculation for increasing amounts of ML fermentation, until we reach our end-point pH without having to alter the SID, or 100% ML fermentation has been achieved.

3.9 Titration curve

1. To change the pH to 8.2, we know that the amount of base required is simply $[M]$, from section 2.3.
2. Divide $[M]$ into, say, 100 equal increments, and calculate the pH for each increment in SID. Use the algorithm outlined below (3.9.1) to determine pH for the various SIDs. Store the pH values in an array.

3.9.1 The pH algorithm

We wish, for example, to calculate the pH that results when we alter the SID by a certain amount. We'll call our starting pH pH$_i$.

Rearranging (7) we obtain:

$$[H^+] + [\text{SID}] - \sum_{x=0}^{5} \left(\sum_{i=1}^{\max(x)} i.[A_x^{i-}] \right) - [OH^-] = 0$$

In a manner analogous to our Stewart tutorial, we can make two guesses, an upper and lower one. Let's play it safe and set the following limits to our guesses. Our lower limit will be the initial pH, pH$_i$ and our upper limit, pH$_{top}$, will simply be 8.2. Our first guess will be the geometric mean of the two ($\sqrt{\text{pH}_i.\text{pH}_{top}}$).

In order to calculate $[OH^-]$ (which becomes significant at a pH of above 7), we note that:

$$[H^+] * [OH^-] = K'_w$$

…where K'_w is the dissociation constant for water multiplied by the molal concentration of water. At 25^oC the value for water is $1.0 * 10^{-14}$.[8]

Now if our guessed value is exactly correct, then our calculation of the left side of the above equation will be exactly zero. If our guessed $[H^+]$ is too high (pH too low), then the result of our calculation will be positive. If the guessed $[H^+]$ is too small, the calculation must be negative.

So we can simply iterate our guessing, achieving a progressively more accurate pH value. In our initial version of the program, we will be unbelievably slovenly, and simply recalculate all ionic species for each pH value, without any attempt at optimisation!

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[8] But note that ideally we should probably adjust this value because of the alcohol present!

4 Java applet

4.1 User interface

The above algorithms suggest a format for the user interface. We will use the rather nasty and cumbersome Java Abstract Windowing Interface (AWT). We will need:

1. A central graph, on which we will plot one of:
    - Malic vs tartaric acid added, to achieve a desired pH;
    - ML fermentation: pH change vs percentage ML fermentation;
    - Titration curve: pH vs added NaOH.

   Axes must be appropriately labelled.

2. Top controls, which might contain initial and desired pH, TA and a 'Calculate' button. We will initially (simplistically and somewhat counter-intuitively!) set things up so that if the desired pH is lower, we present a malic vs tartaric acid curve, if higher, a ML fermentation curve, and if *identical* to the initial pH, a 'debugging' titration curve! A tad clumsy.[9]

3. Bottom controls. These will consist of just six boxes, five of which can be altered. For clarity and user convenience, we will represent the relative amounts of the various species of acid as *percentages* rather than ratios to tartaric acid. We will not allow the user to specify the percentage of tartaric acid, as this simply makes up the balance! (The percentage tartaric acid must still be displayed, for completeness).

4. East and west 'side' controls will for now be left blank. In a more complex version of the applet, they could contain details of wine specific gravity or % alcohol, or perhaps even a choice of Pitzer versus Debye-Hückel calculations, and selection of formulae for calculation of permittivity!

5. It might be reasonable to somewhere have a space for messages, especially error messages.

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[9] We might otherwise consider having a drop-down menu that allows us to select a particular calculation.

4.1.1 Checks

We will have a default value in each box.

We need to check that entered values are 'reasonable'. Such checks might comprise:

1. Initial pH should be between 2.0 and 4.0.
2. Final pH should be between 2.0 and 4.0.
3. Percentages of the various acids should, when added, allow a tartaric acid content of not less than 30%, and maximum values percentage wise of the following acids: malic 50%, succinic 20%, lactic 15%, citric 15%, and acetic 10%.[10]

4.1.2 Anticipated errors

We hope to prevent a lot of calculation errors using the above checks. Our calculations will not require large amounts of memory, so we do not anticipate major errors with arrays overrunning memory, or memory not being provided. Having said this, we note the infinite potential for error in some operating systems, such as MS Windows!

One thing we might consider doing is to have debug facilities where we can examine the concentrations of all ionic species!

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[10] These values are rather arbitrary, and could be varied, but it's difficult to conceive of a real wine with under 30% tartaric acid, or, say, a vast amount of citric or acetic acid!

4.2 Java code for user interface

The java source code is available for download on our web-site. It is rather rough and ready, as it was knocked together fairly quickly. Most of the code would benefit from a good re-write, and we make no claims that the structure of the code in any way represents good Object-orientated programming!

4.3 HTML code

The HTML code for the applet is trivial, and can be viewed in your favourite browser! (Click on View—Source, or the equivalent).

4.4 Questions

We have already listed the assumptions under which we are working. All are important limiting factors, but some perhaps more easily addressed! In particular:

1. Is the PCO_2 of non-sparkling wine really negligible? We should really re-write the above taking CO_2 into account!
2. It would be relatively easy to add calculations that involve various assumed dissociation constants based on the percentage of alcohol present
3. We *must* surely allow conversion between molal and molar concentrations. Check with John — I suspect all winemakers' calculations are molar; we then need to know wine specific gravity too!
4. Are we titrating to pH 7.0 or 8.2?

5 Disclaimer and GPL

This code is released under the Gnu Public Licence (GPL). Please note the conditions of this licence. Note specifically that this project and the associated code are intended to be a learning/teaching exercise, and not for commercial use. If you base your wine-making on the calculations presented here, then you have only yourself to blame if things go wrong. We make no claims or representation that the model presented here accurately or reliably represents what happens in real wine!