

**DRAFT of 2 May 2009**

# **Nearly Universal Brewing Water Spreadsheet (NUBWS) Users Manual**

## **Introduction**

These instructions are for the water analysis spreadsheet first put together for participants in the BURP Water Workshop held in the fall of 2008. It has, since that time, undergone several revisions that include not only correction of errors that came to light but also addition of several new capabilities that were not part of the original. At this writing it represents a tool with which the brewer ought to be able to solve most of the brewing water problems he may expect to encounter. Thus we have named it the Nearly Universal Brewing Water Spreadsheet (NUBWS). The “nearly” means that it doesn’t do everything. Evidence for this is that we keep thinking of things to add to it. Nor is it perfect in what it does do. When something of this flexibility is built “from the bottom up” it is often less organized and the user interface less intuitive than it would be if we had started out with a set of requirements in mind and designed to meet them. Furthermore, laying out an exhaustive test program is a nearly impossible task and we have found errors in the past. Correction of some of these is noted in the revision history at the top center of the spreadsheet. We are constantly testing and searching for errors and omissions, and ask that users inform us at [ajdel@cox.net](mailto:ajdel@cox.net) of any problems or shortcomings they may encounter. We are also receptive to ideas about new capabilities, though, naturally, we cannot promise to incorporate any particular request at a particular time.

### **Acknowledgement:**

I’d like to thank Bill Pierce who acting totally on his own initiative volunteered to edit this manuscript. While he hasn’t seen this particular draft yet he took the previous hodge-podge and made it into something readable for which you, dear reader, as well as I owe him a debt of gratitude.

## **Safety**

The NUBWS, being, as it is, nearly universal will let you do calculations involving chemical materials that you should not be handling unless you are an experienced chemist or brewery worker trained and equipped to properly deal with them. Mother Nature uses hydrochloric, sulfuric, nitric and phosphoric acids when she prepares the water which comes out of your tap and so NUBWS is capable of making calculations involving those acids (or indeed any acid you choose if you know its dissociation constants) and the strong bases sodium and potassium hydroxide but she uses them in dilute form. She does not order drums of fuming sulfuric acid to prepare Burton water and neither should you. When, in the examples given here to illustrate the use of the

NUBWS, we make a statement such as “add sulfuric acid until the proton deficit is 0” we mean to increase the value in the sulfuric acid cell of the spreadsheet – not add battery acid into your tap water. We are not giving recipes here. For the record, *we do not advocate the use of strong chemicals in the preparation of brewing water*. The acid we do recommend, not only because it is readily available to home brewers in safe to handle form but because it emulates what Mother Nature does and thus tends to give good results, is carbonic acid obtained by bubbling carbon dioxide gas through the water being treated.

A general guideline might be that if you can buy something at the super market or your local homebrew shop it is OK to use. This would include the chemicals most often used in water treatment: calcium sulfate (gypsum), calcium carbonate, slaked lime (pickling lime), sodium bicarbonate (baking soda), magnesium sulfate (Epsom salts), calcium chloride, citric acid and lactic acid.

Another consideration is that chemicals you buy from these sources are *food grade* which means not only that potentially problematical impurities are controlled to safe levels (for example most lye is made with mercury and thus usually contains some) but that the material has been handled and packaged on equipment approved for the preparation of food.

We wrap up this section by reminding even the experienced to add acid to water and never do the opposite.

## **NUBWS as Compared to Other Brewing Water Spreadsheets**

There are many water chemistry spreadsheets available on the internet. In fact it seems that every homebrewer with engineering, chemistry or computer science background has prepared one. Most are designed to accept parameters obtained from a laboratory or utility-furnished water report and do some analysis usually at least to the extent of computing residual alkalinity and the resulting expected mash pH shift relative to a distilled water mash. In many users can then input data concerning additions of certain common salts, sometimes acids and sometimes deionized dilution water from which the spreadsheet computes an adjusted water profile by summing the ions added to the ions present in the source water specification. In some spreadsheets this result can be compared to a target ion profile also entered by the user.

So why should you use the NUBWS instead of one of the others? There are 2 main reasons: Accuracy and Flexibility. Starting with accuracy: the NUBWS is the only spreadsheet of which we are aware (and we recognize that there may be ones of which we are not aware) that checks the electrical balance of water profiles to see if they are physically realizable. A spreadsheet that doesn't do this will allow you to try to design a physically impossible water from a source profile for water which never existed. By the latter we mean that just because you have a list of numbers on a piece of paper from a lab or the local water authority doesn't mean those numbers represent real water. This is quite common because of the way in which water parameters are measured and reported.

The main clue that this important aspect of water chemistry is being ignored is that the spreadsheet doesn't ask about the pH of either the source or target water (both must be considered). Part of electrical balance is Proton Deficit which, again as far as we know, only NUBWS considers. By so doing it allows users to either ask for pH shifts (i.e. have target water at a pH different from source) in doing synthesis or see what the consequences of adding acid or base to water will be in terms of its pH. Where only neutral salts of strong acids and bases are involved in additions (sodium chloride, calcium sulfate) or where acids are added to waters of low bicarbonate content ignoring pH does not have major impact. Where additions of carbonates or bicarbonates are involved and/or where the water is highly carbonaceous ignoring pH can have a larger effect on answers obtained.

NUBWS is also more accurate than other spreadsheets we have seen because it recognizes that brewing waters, even though they are dilute solutions, are not *ideally dilute*<sup>1</sup> and so it does not use the chemistry of ideally dilute solutions (unless the user expressly asks it to). NUBWS also is aware that the constants that control the behavior of carbonic acid, bicarbonate ion, carbonate ion and calcium carbonate solubility (and this is 97% of brewing water chemistry) are temperature dependent. These two considerations usually have but small effect on computed results.

The NUBWS has a host of features that others do not to the extent that we hope it truly approaches its goal of being universal (with respect to brewing water at least). The following lists some of things it does.

1. Allows for synthesis of highly carbonaceous waters (e.g. Burton's) by computing the amount of carbon dioxide which must be dissolved to get chalk (calcium carbonate) to dissolve and bring the pH to the desired value. As this emulates what nature does it often results in better (in the sense of close match to a desired profile) match than the use of other acids. Also allows for pH adjustment of any synthesis by use of this most natural of acids.
2. Recognizes that, if bicarbonate content is reported as alkalinity, the pH used as an end point by the laboratory that determined alkalinity when the alkalinity titration was done must be known. This is necessary in order to correctly compute the amount of carbonic, bicarbonate and carbonate species in the water.

---

<sup>1</sup> Ideally dilute solutions are those in which the ions are so far apart that they are independent of one another to the extent that sodium ions, for example, would have no effect on, for example, the solubility of calcium carbonate. In non ideally dilute solutions the converse is true and adding more sodium to a solution will make calcium carbonate more soluble.

3. Can be used to determine the amounts of salts, acids or bases to be added to a sample to bring about a particular pH shift or the pH shift that results when salts or acid are added to a sample.
4. Computes saturation with respect to carbon dioxide, calcium carbonate and calcium hydroxylphosphate (apatite) to give the brewer insight as to how stable a particular water is and allow him to answer questions such as “How likely is it that boiling will be an effective means of reducing the alkalinity of this water?”, “Will the pH of this water change over time if it is allowed to stand exposed to the atmosphere?” and “What would the pH of this water be if I put it in a Cornelius keg under 14.7 psig carbon dioxide and how many volumes of  $CO_2$  would it contain?”
5. Computes the amount of lime that would be required to decarbonate a water sample using the split or straight lime treatment method.
6. Can do dilution computations with water with an arbitrary ion profile. This means that if, for example, you have alkaline water and wish to reduce its alkalinity by blending with bottled water of known composition, the NUBWS can calculate the properties of the resulting blend, including pH shifts. You may, of course, also use deionized water. You simply specify 0 ion content in the portion of the spreadsheet where the dilution water is described.
7. Allows the user to design buffers and see what the effect of adding them to his water would be. Data on acids and the sodium and potassium salts of citric, phosphoric, lactic, and tartaric acids are included. The brewer may add 2 other acids of his choice (he must know its pK's).
8. Is setup to allow considerable use of the Excel Solver to obtain answers to questions that require iterative solution. An example of this would be simultaneous adjustment of multiple salt and acid quantities to minimize the difference between a synthesized and desired ion profile. This may be the feature that is of greatest practical value to the user.
9. Has flexibility with respect to the criterion used to match a mix of source water plus salt/acid/base additions to a desired profile. In particular the participation of individual ions being matched can be weighted so that, for example, if matching sulfate is more important than matching sodium the former can be given a large weight (e.g. 100) and the latter a small one (ultimately 0 if it is a real “don't care”). Errors (to be minimized by Solver) are either rms mg/L or rms p values (see Appendix A for definition of p operator).

Thus there are a wealth of features, the effects of which, if they were ignored, might or might not be significant depending on the application. The philosophy here is that as the cumbersome math associated with all of these is conveniently hidden from, though still

available to the user, he might as well avail himself of the potential for improved accuracy. In other words, why not have the best available if it requires no additional effort on the user's part? But of course there is nothing in this world worth having that does not come with a cost. In this case it is complexity. The NUBWS is large. It spans 48 columns and 157 rows (though there are lots of unused cells). It asks for data on things like sample temperature, sample pH, the pH to which the sample was titrated when its alkalinity was measured, and the pH at which the synthesized water (i.e. the source water as modified by addition of salts and acids) is desired. In some cases this information may not be readily available and educated guesses must be supplied. Note that spreadsheets that do not ask about these things are either ignoring their effects or assuming a value for them.

NUBWS floods the user with information, some of which may not even be familiar and requires that he know how to interpret what he sees and what is important and unimportant for his application. It is the task of these instructions to provide enough information that the user can use the spreadsheet to answer his brewing water questions. While many explanations of how things work are given, perhaps the examples are the best way of learning to use NUBWS. Keep in mind that you don't *have* to understand how any of it works, but you do need to know how to feed it what it needs and how to interpret what it gives back. If you do make the effort to learn something of its workings (and there is material on that available in the Appendices), you will find it can teach you a lot about brewing water chemistry.

We will start with a description of the spreadsheet area by area. There are five of these – one each for entry of Source, Target and Dilution water parameters, one where salt, acid and dilution water additions are specified and the modified water characterized, and the fifth compares Target water to the synthesis that results from additions so the user can see how close he came to his goals. In the descriptions individual cell contents are discussed. The heavy duty chemistry is in Appendices.

When looking at the examples, you should definitely enter them into the spreadsheet to gain familiarity, but you should also do lots of “what if” experimentation by tweaking various input parameters in order to see what happens when you do. This is the best way to gain familiarity with the spreadsheet and brewing water chemistry.

## **General Comments on Use**

The NUBWS and these instructions can be downloaded from [www.wetnewf.org](http://www.wetnewf.org). Because the spreadsheet is large you might want to consider printing these instructions so you can refer to them while the spreadsheet is on the screen, as you might find that easier than constantly shuffling windows, and you can write notes on the hard copy, etc.

The spreadsheet accepts inputs in white cells and puts results in colored cells. As you get the NUBWS from the website all cells except the white cells are protected. You may unprotect the spreadsheet (no password is required), but if you do be sure not to enter anything into a colored cell. Be sure you have a backup copy of the spreadsheet that you

can use if you accidentally change one of its formulas and don't realize this until it is too late to save the situation with the Undo function. You will have to unprotect the spreadsheet if you wish to use the Solver.

The spreadsheet has five main areas labeled Source Water, Target Water, Dilution Water, Synthesis and Synthesis Quality. Source Water, Target Water and Dilution Water are the same and are for the entry of water parameters with the Source Water area at the far left, the Target Water area just to the right of the Synthesis area and the Dilution Water area at the far right hand side of the spreadsheet. Between the Source and Target areas is the Synthesis section in which the user specifies amounts of salts and acids to be added to the source water in order to approximate the target water. The parameters of the modified water are displayed in this section. The Synthesis Quality section, between the Target and Dilution water areas, compares the parameters of the modified water to the parameters specified for the target water. This lets the user see how close his synthesis is to the desired target.

There are also five auxiliary areas at the bottom of the spreadsheet. One each below the Source Water, Target Water, Dilution water and Synthesis areas is for computation of ionic strengths, total carbo, distribution fractions and minus the log of the average activity coefficient,  $pfm$ , which are computed iteratively. These areas are labeled "Source ionic strength and activity coefficient calculation", "Synthesis ionic strength and activity coefficient calculation", "Target ionic strength and activity coefficient calculation" and "Dilution water ionic strength and activity coefficient calculation". Do not enter anything in these areas (they have no white cells). A fifth auxiliary area, found below the Synthesis area and labeled (in an included text box) "Acid Data", is for storage of data on lactic, citric, tartaric and phosphoric acids, and for the entry and storage of data on other weak acids and their salts as chosen by the user.

In these instructions a single cell will be described by its coordinates. For example, C2 means the cell at row C column 2. A range of cells will be described by a similar notation. For example, (A:H,1:71) includes all cells in Columns A through H and rows 1 through 71.

Though you may not fully appreciate what the following means until you are more familiar with the NUBWS, the general instructions for use can be stated in two sentences: *Enter the parameters of the water you have available, the water you will use for dilution (if you plan to do that) and the water you want to realize, monitoring the electrical balance for each as you do so. Enter dilution water, salt and acid additions, monitoring proton deficit as you go, until the synthesized water matches the desired water as closely as possible.*

The last paragraph does not touch on the several other things you can do with NUBWS such as determining the amount of acid or base needed to shift the pH of a water from one pH to another or the design of buffers. For those applications the general instructions might be: *Add acid, base or salt(s) and then set the proton deficit to 0 by changing target pH or set target pH and then zero proton deficit by adding acid, base or salt(s).*

Also part of the general instructions should be a note about use of results calculated by the NUBWS and the example of acidification of a given water to a particular pH is good with respect to this aspect of its use. To do this calculation you must tell NUBWS the alkalinity and pH of the water you wish to modify and the strength of the acid you wish to use. In return NUBWS will tell you how many mL of acid of this strength you should add to a specified volume of water to get the desired pH. There will be errors in the value of alkalinity, pH, acid strength and water volume (all these are measured by someone and measurement is always subject to error). Thus the answer calculated by NUBWS will be in error by an unknown amount. The way to get around this in the case of the acid addition example is to measure out the amount of acid calculated by NUBWS plus a little more and then add it in increments to the water being, monitoring pH, until the desired pH is reached. There should be some extra acid which can be discarded (safely).

With salts you can't really use this incremental approach so all you can do is add the calculated amounts and then analyze the resulting water or have it analyzed. Here it is not so critical. If your Burton water has an alkalinity of 190 instead of the 200 you had intended it is still essentially Burton water.

## **The Solver**

Microsoft used to furnish a tool called the Solver with all versions of Excel. Because the Solver worked through Visual Basic and Visual Basic Assistant, which posed a security threat, it has been removed from some releases of Excel. For example, the 2008 version of Excel for Macintosh does not have it, though its manufacturer makes an outboard version available to Mac users through their website at <http://www.solver.com/mac/>. The situation is unclear at this point. Rumors about the future of VBA are not consistent.

To see if you have Solver, look for it in the Tools Menu. In some older versions of Excel, while it was furnished with the install disk, it was not installed as a part of the normal setup and required a separate installation.

To use the Solver the spreadsheet must be unprotected. To change the protection use the "Protection" entry in the Tools menu.

To see how the Solver works, type 1 into cell A1 on a Solver-capable Excel spreadsheet (not the NUBWS) and put "=tan(A1)" in cell A2. This cell (A2) should display 1.5574, which is the tangent of 1 radian. Now suppose we want to find the value for cell A1 that would make A2 contain 1, i.e. the arctangent of 1. If we enter 0.7 we see 0.84229 and if we enter 0.8 we get 1.0296. Thus the right answer is between 0.7 and 0.8. By groping about we can find, after a few trials, that 0.7855 gives the answer 1.000203. If, however, put 1 back in A1, bring up the Solver and ask it to set A2 to 1 by varying A1, it immediately calculates 0.7853981225. A2 will read 0.999999924 (the Solver's accuracy can be modified to get even closer to 1). On the other hand if, we put 7 into A1 and ask the solver to set A2 to 1, it will, in this case, give 7.068583356 in A1 and A2 will read

0.99999977, again very close to 1. This is a valid solution (there are infinitely many more, as the tangent is a periodic function).

This simple example illustrates some essential features of the Solver. It can be used to automatically find solutions where manual trial and error works but is tedious. The obvious place where this is valuable in a water spreadsheet is in specification of salt additions in trying to match a particular ion profile. Here multiple parameters (the amounts of several salts chosen by the brewer) are automatically tweaked while trying to minimize the sum of the squares of the differences between desired and realized ion concentrations. Fuller details are to be found in the description of the use of the Synthesis and Synthesis Quality parts of the NUBWS.

The simple example showed that there may be more than one solution – in the case of the arctangent all are equally good, i.e. they all get the value of the tangent very close to 1. In the brewing water chemistry domain not all solutions are equally good. The Solver will not necessarily find the best. It usually finds the one closest to the starting point. The Solver doesn't know anything about chemistry. It only knows about numbers, so if it finds a solution that requires you to add -10 mg/L of some salt it will happily report this solution to you. This last dilemma is avoided by setting constraints in the Solver that require the amounts of all salt and acid additions to be greater than or equal to 0. Convergence to a good solution is aided by manually specifying salt additions to get a rough solution and then letting the Solver refine it. The examples in these instructions should make it clear how these things are done. Finally, the user should examine all Solver solutions to see if they are reasonable.

## **Source Water Area**

The source water area is a light cyan color and is located at (A:H,6:77). The region (B:D,85:126) is where ionic strength calculations are made for the Source Water. In this area (A:H,6:77) the user enters what he knows about his available water and the spreadsheet interprets it. The analysis converts values usually specified in units other than mg/L to mg/L values for use by the Synthesis Area, and also checks to see whether the water report represents physically realizable water (often it won't) and whether the water is under- or over-saturated with respect to carbon dioxide and calcium carbonate.

Usually the user will be entering data on mineral content as reported by a water supplier or a testing laboratory. As this data is often incomplete or corrupt in some other way, this often leads to problems. We will identify some of these problems and suggest ways of working around them.

## **Ideal/Non-Ideal Solution Chemistry**

Before using the spreadsheet for any purpose you must tell it whether you want it to use the chemistry of “ideally dilute solutions” or to attempt to model, to some extent, the

effects caused by the fact that no solution is, in reality, ideally dilute. “Ideally dilute” means that the ions dissolved in the solution are so few and far between that they do not interact with one another electrically. Thus the sodium ions in an ideally dilute solution would have no effect on the precipitation of calcium carbonate. In the non-ideal solution the converse is true. Ions are numerous enough that they do interact and sodium ions will have an effect on the precipitation of calcium carbonate (and other reactions as well). We will return to this point when saturation is discussed later.

All other brewing water spreadsheets known to the author use the ideally dilute model. The water industry, in general, does not, though its treatment of non-ideal solutions is somewhat simplified (see Appendix A). Thus you may wish to select the non-ideal option in the hopes of getting “better” answers (though the differences between ideal and non-ideal answers will be small), or the ideal option in order to be in line with what most other spreadsheets would calculate. The selection is made by typing a 1 in C7 for the ideal model and a 0 for the non-ideal model.

## **pH**

pH is often referred to as “the master variable” because everything else in water chemistry depends on it to some extent. This is particularly true with respect to the chemistry of weak acids such as carbonic acid and its salts which are of critical importance in brewing water chemistry. In order for the spreadsheet to be able to properly interpret alkalinity information, it must know both the pH of the water sample and the pH to which it was titrated in the laboratory when its alkalinity was measured. Read Appendix B, Alkalinity for an explanation of what alkalinity is, how it is measured, the significance of End Point pH and what value to enter. It is important that you read that material at some time for full appreciation of how the NUBWS works, but if you would prefer to do that at some later time you may proceed now by entering 4.3 in D8 for the End Point pH unless your water report clearly indicates that a different pH was used, in which case that value should be entered.

## **Temperature**

The spreadsheet needs to know the temperature at which the laboratory measurements were made because all the constants it needs to calculate carbo system parameters are temperature dependent. Enter the sample temperature in C9 using a positive number for Celsius and a negative number for Fahrenheit. Clearly, you cannot enter a temperature of less than 0 °C or 0 °F. Irrespective of whether the input to Cell C9 is Fahrenheit or Celsius, the Celsius temperature is displayed in D9. The temperature dependent parameters are displayed below the temperature in Col C. These parameters and their roles in water chemistry calculations are explained in Appendix A.

## **Form of Calcium Carbonate**

A number, 0, 1 or 2, is entered in C14 to tell the spreadsheet what form of solid calcium carbonate you wish it to use in calculating saturation. If 0 is entered it will use the

solubility product for calcite, the most common but least soluble (and most stable) form. 0 should be used unless you are aware that aragonite (enter 1) or vaterite (enter 2) are forming or you are curious as to what the effects of these more soluble forms might be. The label in B15 indicates the name of the form according to the number you enter.

## Alkalinity

Here (C26) you will enter information about your water's carbonic/bicarbonate/carbonate content. You do this either by entering an alkalinity or a total carbo (sum of carbonic, bicarbonate and carbonate) number. In most cases you will be entering an alkalinity number from a water report, in which case an 'A' should be placed in A26 to signal this to the spreadsheet. Alkalinity values in the US are nearly always reported in ppm as  $CaCO_3$ . If this is the case, enter the value as a positive number. Should alkalinity be given in milliequivalents per liter (sometimes called millival), enter the value as a negative number. Thus +100 and -2 represent the same level of alkalinity (1 meq/L is equivalent to 50 ppm as  $CaCO_3$ ). This can be verified by entering each of those values while monitoring the summary data in (C,61:62).

Note that 0 alkalinity is an impossibility (unless the sample pH and end point pH are the same -- see Appendix B for an explanation). If you enter 0 alkalinity the spreadsheet will interpret this to mean that the water contains no carbo. C61 will display the alkalinity of a 0 carbo water with the specified end point and sample pH in such cases. In cases where there is no carbo, such as where you are specifying de-ionized water as the source water, it is better (as a matter of self discipline -- the NUBWS will give the same results in either case) to enter 'C' in A26 and 0 in C26.

If 'C' is entered in A26, any number entered in C26 (must be positive numbers) is interpreted as the sample's total carbo in units of millimoles/L. This is the sum of the mmol/L carbonic, mmol/L bicarbonate and mmol/L carbonate. The corresponding alkalinity will be calculated (based on sample and end point pH's) and displayed at C61 (in mEq/L) and C62 (ppm as  $CaCO_3$ ).

Once an A or C value has been entered the spreadsheet can calculate and display amounts of total carbo (A input) or alkalinity (C input), and the amounts of carbonic acid, bicarbonate ion and carbonate ion. These are displayed in Col C Rows 32 through 39. The numbers labeled "Rough" are first guesses at the actual values based on the ideally dilute solution model irrespective of which model has been chosen in C2. As explained in Appendix B, refined numbers must be obtained iteratively and these are displayed in rows 37 - 39. When the non-ideal model is used if anything is dissolved in the water, the rough and refined numbers will be slightly different. Also note that the carbo species distribution (and even total amount of carbo displayed in C31) will change according to how much of other (non-carbo) ions, for example, sulfate, are present when the non-ideal model is selected. This is because the carbo quantity is calculated from the entered alkalinity and the calculation (see Appendix B) depends on the solution's ionic strength which in turn depends on the concentrations of all charged species it contains.

## Hardness

Hardness is, by definition, a measure of the concentration of each of two, and only two<sup>3</sup>, dissolved metal ions – those of Calcium and Magnesium. You enter data about their concentrations in C27 and C28. Calcium and magnesium concentrations are sometimes reported in units of milligrams/L of the metal itself (the report is often marked “as the metal” or “as the ion”) but more frequently in “ppm as calcium carbonate” – the same units as alkalinity. To enter “as the metal” use negative numbers. To enter as ppm as  $CaCO_3$  use positive numbers. Whichever you use, the concentrations in milliequivalents per liter are displayed in C30 and C31, respectively, and the amounts as the ion in A30 and A31.

A summary of the hardness information is also given in Col. C rows 63 – 67. Here both hardnesses are displayed as calcium carbonate, as is the total hardness, also as  $CaCO_3$ . The *temporary hardness*, which is equal to the alkalinity if total hardness is greater than the alkalinity, and the total hardness otherwise (i.e. it is the amount of calcium and/or magnesium carbonate that could conceivably form if the water were boiled), is also given in C60. Waters with high temporary hardness will likely turn milky with precipitated lime if they are heated. The *effective hardness*, which is the calcium hardness plus half the magnesium hardness (see Residual Alkalinity), is also displayed in C62.

### Sulfate, Chloride, etc.

Cells C32 through C52 are for the entry of the concentrations of other ions commonly found and reported in potable water. All are to be entered in units of mg/L. Note that sometimes nitrate and nitrite will be reported in units of “as nitrogen,” in which case the value should be multiplied by 4.4 to obtain mg/L as the ion. Iron is reported according to its oxidation state, usually in terms of total iron and “clear water” or Fe(II) iron. In such cases Fe(III) iron concentration is the total concentration less the clear water Fe(II) concentration.

### Source Area Calculated Parameters

Computed results are presented in Rows 58 through 77. Most important of these is the Electrical Imbalance expressed in mMol/L in F54 and as a percentage in F55, but Residual Alkalinity in C68 and C69 is more familiar to and of more interest to the brewer.

---

<sup>3</sup> Where, for example, strontium is present, as it is in some waters, though usually at sub ppm levels, it will effect the values of hardness measured by the usual method of EDTA chelation (but not atomic absorption spectrometry). Iron has a similar effect but is also usually found at sub ppm levels. The NUBWS does not does not adjust hardness entries for either iron or strontium.

**Balance/Neutrality:** Water is electrically neutral. This means that for every charge on an anion (e.g. chloride, bicarbonate, etc.) there must be a matching amount of charge on a cation (e.g. sodium, hydrogen, potassium, etc. ions). NUBWS calculates the ion concentrations from the data you enter and tallies total cation charge (F58) and anion charge (G58). These should be equal in magnitude, but for that to happen every piece of data furnished must be precisely correct and every species of ion in the water must be accounted for. That does not represent the real world and finite imbalances are to be expected. The amount of the imbalance is a measure of the quality of the input data. It is reported as the difference in anion and cation concentrations in F59 and as that difference divided by the sum expressed as a percentage in Cell F60. Good analysis reports will provide accurate measurements of the concentration of every ion found in the water in appreciable quantity, and the measurements will all have been made from the same sample in which case the percentage imbalance will be small. This is in contrast with the typical municipal water report in which the given values may be averages over some period of time such as a week or month and some ions may be measured from samples taken on days different from those on which samples for other ions were taken).

The Source Water area reproduced below holds data from a report issued by a laboratory frequently used by home brewers. End point pH was not given in the report, so we used the methyl orange endpoint of 4.3 that is commonly used in brewing. We used 20°C as the analysis temperature. This was also not given in the report but makes very little difference in the final results and is close to room temperature. We chose not to use the ideally dilute treatment, although we have no idea whether this laboratory does that or not. Alkalinity was reported as calcium carbonate but the hardnesses were reported as the ion, hence the negative signs preceding the entered values.

The spreadsheet calculates the cation total as 1.440 mEq/L and the anion total as 1.116 (Row 58), which is an imbalance of 0.324 amounting to over 10% of the total ion concentration. This is not deemed very good performance, so the fields that list the imbalance data are highlighted in red. The report itself gives 1.4 and 1.1 as the values (only 1 decimal place) and thus the calculations done by the laboratory are not terribly different from the NUBWS's. We will have some suggestions as to what to do about this imbalance after we complete discussion of the spreadsheet's layout.

**Alkalinity and Hardness:** Below the imbalance data we find, in Col. C, a summary of the hardness and alkalinity calculations. The Alkalinity values in (C,61:62)) are copies of the of the input alkalinity value when A21 is set to 'A', but represent the value calculated from total carbo in cell C26 when A26 is 'C'. The hardnesses are also copies of (C,27:28) when the inputs are ppm as  $CaCO_3$ , but are calculated from 'as the ion' inputs when the data are, as in this example, in that form. They are always displayed here "as calcium carbonate". Their sum is the total hardness, of which in this example 25 ppm (equal to the alkalinity in this case) is seen to be temporary. This is the amount that might be expected to precipitate on heating, though it is unusual for there to be any precipitation unless the temporary hardness is greater than 50 (See Appendix C for details).

The effective hardness is explained under Residual Alkalinity.



alkalinity will be canceled by the protons released when the given amounts of calcium and magnesium react with malt phosphate, so that the pH of a mash containing 3.5 mEq/L calcium for each mEq/L bicarbonate would have the same pH as a distilled water mash. The part of the bicarbonate not “balanced” by calcium and phosphate Kohlbach called “residual alkalinity” and it can, given his statement above, be simply calculated from

$$RA = alk - ([Ca^{+2}] + 0.5[Mg^{+2}]) / 3.5$$

where the terms in brackets are the ion concentration *in the same units as the alkalinity*, i.e. either ppm as  $CaCO_3$  or mEq/L<sup>4</sup>. Note that this is different from our previous use of brackets that have signified concentration in mol/L. Naturally residual alkalinity is in the same units as alkalinity (and the ion concentrations).

It is instructive to compare the RA of a sample against the RA’s of well-known brewing cities. This is done by plotting the alkalinity for each sample we have for a given city against one-half the magnesium hardness plus the calcium hardness. Kohlbach called this quantity the *effective hardness* and it is so labeled in the spreadsheet where it is displayed at C67. Figure 1 is such a plot. The diagonal lines are lines of constant RA and are labeled with the RA values and the expected pH of a mash made with a water sample that plots close to a line. In our example from above the alkalinity is 25 and the effective hardness 45. This plots about halfway between the RA=0 and RA = 25 lines and thus the water has an RA of about 12.5 (the spreadsheet calculates 12.08). The RA labels also contain pH numbers that are the expected pH of a mash made with the water in question under the assumption that a distilled water mash would come in at pH 5.75. The RA = 25 line lists 5.79 as the pH, so we would expect a pH of 5.75 for water halfway between the 0 and 25 lines. Rather than list a particular pH the spreadsheet calculates a shift of 0.02 pH (Cell C65) consistent with the chart. This shift is 0.00168 pH per ppm as  $CaCO_3$  or 50 times this i.e. 0.084 pH/mEq-L<sup>-1</sup>. The reciprocal of this, 11.905 mEq-L<sup>-1</sup>/pH is, according to Kohlbach (Ref.2), the buffering capacity of the typical pale malt mash. We will be comparing this to the buffering capacity of chemical buffers in Problem 4.

The location of the sample water plot closer to Pilsen than London or Dublin on the chart tells us right away what sort of beer this water, untreated, might be best suited for. It also give a rough idea as to what we might have to do to obtain water like London’s (increase effective hardness to around 250 and alkalinity to around 100).

---

<sup>4</sup> The as  $CaCO_3$  are consistent with Kohlbach’s statement because ppm as  $CaCO_3$  are simply 50 times the milliequivalents per liter.

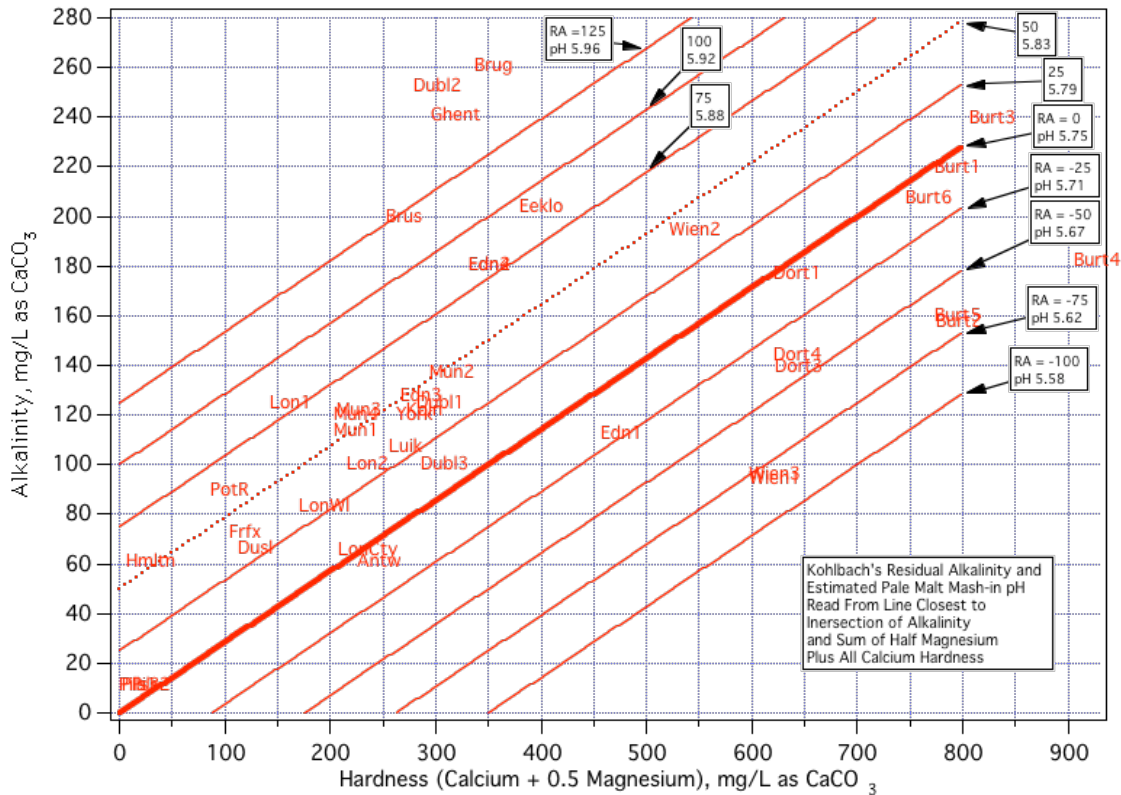


Figure 1 Kohlbach's Residual Alkalinity

Residual Alkalinity, in mEq/L (C64), is the amount of acid that needs to be added to a mash per liter of liquor utilized to neutralize the alkalinity that is not neutralized by acid released by the calcium/magnesium/phosphate reaction. See Addition of Acid in Appendix C for more details.

**Stability:** Salts of calcium are of limited solubility. In particular, water cannot hold much calcium carbonate or calcium hydroxy phosphate (apatite). In addition, water can hold but a limited amount of carbon dioxide. While these statements are true at equilibrium, it may take a long time for equilibrium to be reached and a water sample may well be "super saturated" with respect to calcium carbonate, carbon dioxide or both (discussion of phosphate will be deferred to when we deal with the Synthesis Area).

The spreadsheet happily allows calcium carbonate and carbon dioxide levels well above saturation, that is, it considers equilibrium within the solution but not with the surroundings. Thus a solution supersaturated with carbon dioxide will lose it to the air (it may even fizz) and as it does so its pH increases. A solution supersaturated with calcium carbonate will precipitate chalk and as it does so its pH will decrease. For example, the water in Screenshot 1 is supersaturated with respect to  $CO_2$  but undersaturated with respect to  $CaCO_3$ . This sample was from a well, and well water is typically supersaturated with respect to  $CO_2$  because soil bacteria respire, thus producing a subterranean partial pressure of this gas orders of magnitude greater than its partial

pressure in the atmosphere. Over time we would expect the pH of this sample to increase from its reported value of 6.7.

The NUBWS treats calcium carbonate in ways representative of how it is treated by the water industry. In particular it computes the pH at which the water is saturated with calcium carbonate given the amount of calcium and carbon in the water. This is called the *saturation pH* and is displayed in cells C72. The *saturation index*, SI, is simply the difference between the sample pH and the saturation pH. It is one of several indices used by the water industry mostly to predict whether their mains will be occluded, corroded or protected. If a sample has a pH higher than its saturation pH, the saturation index will be positive and it will precipitate calcium carbonate. The cells that display saturation pH and SI will turn red to signal this condition. From the point of view of the water company, a modestly positive SI is desirable, as this will result in gradual deposition of  $\text{CaCO}_3$  on the inside of their mains, which will protect the pipe from corrosion. A large positive SI, on the other hand, will result in faster deposition to the point that the pipe may become occluded.

If the sample pH is lower than the saturation pH, the saturation index will be negative and any solid calcium carbonate to which the solution is exposed (such as the coating of  $\text{CaCO}_3$  on the inside of a water main) will dissolve, thus exposing the material of the main itself to the water and increasing the probability of corrosion.

Cells C75, “CaCO<sub>3</sub>: Undersaturated by” or “CaCO<sub>3</sub>: Supersaturated by” or “CaCO<sub>3</sub>: Saturated” display the under- or oversaturation of source water, target water or synthesis with respect to  $\text{CaCO}_3$  in *p* units. As these are the same units as pH, the magnitude of this number should be the same as the SI, and we may eventually remove this cell, as it communicates no new information. It is, however, calculated in a different way than SI.

From the brewer’s perspective, the SI yields information about the stability of the water. A large positive SI indicates that chalk will likely be deposited when the water is warmed in the HLT or in the mash tun or kettle. This is something to consider when using the NUBWS for design of hard, carbonaceous waters. You may wind up going to considerable trouble (see Synthesis Area) to dissolve the minerals called for in the profile only to have them left behind in the HLT. Of course this will also happen to a real brewer using the water you have emulated, and it may be your desire to have things go for you as closely as they would for him as possible. On the other hand, one is tempted to ask why one bothers to put something into the water that is only going to come out again.

If there is no calcium in the water, then the calcium carbonate saturation calculations become confused and all related cells display “#NUM!”

With respect to  $\text{CO}_2$  the NUBWS works slightly differently. It calculates the partial pressure of  $\text{CO}_2$  that one would have to apply over the water in order for the amount of carbonic acid in it to remain in equilibrium. As the atmosphere contains  $\text{CO}_2$  to the extent of 0.0003 atmospheres, any partial pressure displayed in C75 that is greater than

0.0003 represents water that is supersaturated with respect to  $CO_2$  (this will be signaled by the cell turning red), which can be expected to leave the water with a corresponding rise in pH. How this works is discussed in some detail in Appendix B under Reducing Alkalinity – Addition of Acid.

We reiterate that the NUBWS does not calculate the amounts of  $CaCO_3$  that precipitates or of  $CO_2$  that escapes. One can use this to advantage to answer questions concerning things like how much  $CO_2$  will dissolve in water at a given  $CO_2$  pressure and what the water pH will be (see Problems).

Cell C77 displays the number of volumes of  $CO_2$  contained in a liter of water, that is, the liters of  $CO_2$  that would be collected at STP ( $0^\circ C$ , 1 atmosphere) if all the dissolved  $CO_2$  were driven from 1 L of the water sample. Note that  $CO_2$  is 8-12% more soluble in water than it is in beer, so 90% of the value that appears in Cell C77 is a rough approximation of the number of volumes found in beer  $CO_2$  tables at the temperature in C9 and pressure in C75. Note that this pressure is in atmospheres absolute (each atmosphere corresponding to 14.696 psi). Thus 1 atmosphere in one of these cells represents 14.696 psia or 0 psig. To set the pressure in C75, set A26 to 'C' and then adjust C26 until the desired pressure is reached.

See Appendix A for details on carbon dioxide and calcium carbonate saturation and Appendix D for details on calcium phosphate saturation.

**Lime Treatment Trial  $Ca(OH)_2$ :** C75 displays the amount of slaked lime that would be added to 1 liter of the source water if attempting to decarbonate it using lime treatment. It is calculated as the amount of lime (slaked) that could combine with the carbon dioxide in the sample plus that which could combine with the temporary hardness part of the bicarbonate. See the details of how this all works and how to carry out lime treatment in Appendix C.

If you will be using quick (burnt) lime instead of slaked lime, multiply the values given in Cells C76 by 0.757 to get the required quick lime amount.

### **Modifying the Source Water Report**

As we indicated above, one cannot use an imbalanced source report as the basis for a synthesis. If after entering data on source water, (F:G, 58:60) show any imbalance, then the report does not reflect physically realizable water because all real water is electrically neutral. You will never receive a report that balances perfectly because even if there are no other causes there will be errors in measurement, however small, that throw the balance off. To use unbalanced water as a basis for synthesis you should “fudge” the numbers to get neutral water, and in cases where the errors are small you are on pretty solid ground in doing this. Where errors are larger, as in the water in Screenshot 1, you

still must fudge for zero balance, but this may not be easy to do and any synthesis based on the source is suspect.

For example, the water in Screenshot 1 shows a surfeit of cations and a dearth of anions. We can get it to balance by increasing the one, decreasing the other or some of each. But which should we increase or decrease? It might seem that the combination of increases and decreases would be best, and this is what we have done in Screenshot 2 below. Doing this does not repair the problem. You have been given bad data and cannot expect to guess what the error sources were with any reasonable probability of success. Thus you cannot expect to get a very accurate synthesis using this water as the source water unless the additions of salts are so large as to essentially swamp the original ion content of the original water as might be the case for highly mineralized syntheses such as those of Burton or Düsseldorf.

### **Other Uses of Source Water Area**

The Source water area can be used to do more than simply analyze water. It can be used, for example, to determine how much acid would be needed to bring a given water to a different pH. The alkalinity calculation does exactly that displaying in C1, how much acid, in mEq/L is needed to bring the water to the pH entered in D8. To do this we need to get the spreadsheet out of the mode where it copies the alkalinity we enter in C26 to the mode where it calculates it from a carbo value placed there. Continuing with the example of Screenshot2 copy the “Refined Carbo” number from C36 into C26 and change the ‘A’ in A26 to a ‘C’. After changing to ‘C’ all other numbers other than in C26 should be the same as they were before. Now enter the pH of interest in D8. If, for example, 8 is entered, the alkalinity in C61 changes to -0.2849 telling us that 0.2849 milliequivalents of protons need to be absorbed for each liter of water to change its pH to 8. If we had a 1N<sup>5</sup> solution of sodium hydroxide available we would need to add 0.2849 mL of it for each liter of water to be treated.

The Source Area can also be used to synthesize waters with desired ion contents simply by typing in the desired ion contents subject to the condition that F59 is zero. This is handy for “what if” experiments in the NUBWS. For example, if we wanted to see what the effects of water with 100 ppm alkalinity might be on a particular buffer we simply type 100 in C26 with A26 set to ‘A’ and then add some cations to balance (zero F59). We don’t actually prepare waters synthesized in this way i.e. no salt addition calculations are made.

---

<sup>5</sup> A 1 N (read “1 Normal”) solution of acid or base contains 1 equivalent of, respectively, hydrogen ions or hydroxyl ions. One mole of sodium hydroxide which weighs 40 grams, contains 1 equivalent of hydroxyl ions and so 1L of a solution with 40 grams of sodium hydroxide in it would make a 1 N solution.

|    | A  | B                                  | C              | D            | E                     | F             | G            | H          |
|----|----|------------------------------------|----------------|--------------|-----------------------|---------------|--------------|------------|
| 6  |    | <b>SOURCE WATER</b>                |                |              |                       |               |              |            |
| 7  |    | Treat as Ideal? 1 = Y, 0=N         | 0              |              |                       |               |              |            |
| 8  |    | pH                                 | 6.7000         | 4.300        | <b>End Point pH</b>   |               |              |            |
| 9  |    | Temp + for C, - for F              | 20.0           | 20.0         | Temp, C               |               |              |            |
| 10 |    | Temp K                             | 293.20         | 293.20       |                       |               |              |            |
| 11 |    | pK1                                | 6.38           | 6.38         |                       |               |              |            |
| 12 |    | pK2                                | 10.38          | 10.38        |                       | 1.90794       |              |            |
| 13 |    | pKw                                | 14.16          |              |                       |               |              |            |
| 14 |    | Form of CaCO3 (0,1,2) -Use 0       | 0              | 14.16        |                       |               |              |            |
| 15 |    | pKs for Calcite                    | 8.45           |              |                       |               |              |            |
| 16 |    | pKhy                               | 1.41           |              |                       |               |              |            |
| 17 |    | A                                  | 0.506          |              |                       |               |              |            |
| 18 |    | r1 (pfm = 0)                       | 2.0812         | 0.01         |                       |               |              |            |
| 19 |    | r2 (pfm = 0)                       | 0.0002         | 0.00         |                       |               |              |            |
| 20 |    | f1 (pfm = 0)                       | 0.3245         | 0.99         |                       | Bicarb. @ pHa | [H+] @ pHa   | Difference |
| 21 |    | f2 (pfm = 0)                       | 0.6754         | 0.01         |                       | 0.008         | 0.050        | -0.042     |
| 22 |    | f3 (pfm = 0)                       | 0.0001         | 0.0000       |                       |               |              |            |
| 23 |    | f_ammonium                         | 0.9981         | 1.0000       |                       |               |              |            |
| 24 |    | No carb alkalinity                 | 0.0500         |              |                       |               |              |            |
| 25 |    | <b>C or A</b>                      |                |              |                       |               |              |            |
| 26 | A  | Alk, + as CaCO3, - mEq/L           | 35             |              |                       |               |              |            |
| 27 |    | Ca, + as CaCO3, - as mg/L          | -10.00         |              |                       |               |              |            |
| 28 |    | Mg, + as CaCO3 - as mg/L           | -4.00          |              |                       |               |              |            |
| 29 |    | Alk, mEq/L                         | 0.70000        |              | Gram Eq, Wts          | Cations       | Anions       |            |
| 30 | 10 | <-- mg/L Ca mEq/L-->               | 0.50           |              | 20.04                 | 0.499         |              |            |
| 31 | 4  | <-- mg/L Mg mEq/L-->               | 0.33           |              | 12.15                 | 0.329         |              |            |
| 32 |    | Rough Carbo                        | 0.97397        |              |                       |               |              |            |
| 33 |    | Rough Carbonic                     | 19.60          | 59.92        | 62.03                 | 0.000         |              |            |
| 34 |    | Rough Bicarbonate                  | 40.14          | 0.49         | 61.03                 |               |              |            |
| 35 |    | Rough Carbonate                    | 0.01           | 0.00         | 30.02                 |               |              |            |
| 36 |    | <b>Refined Carbo, mMol/L</b>       | <b>0.95713</b> |              |                       |               |              |            |
| 37 |    | H2CO3, mg/L                        | 18.68          |              | 62.03                 |               |              |            |
| 38 |    | HCO3-,mg/L                         | 40.03          |              |                       |               | 0.656        |            |
| 39 |    | CO3--,mg/L                         | 0.01           |              |                       |               | 0.000        |            |
| 40 |    | H+, mmol/L                         | 2.09E-04       | 5.22E-02     |                       | 0.000         |              |            |
| 41 |    | (OH)-, mmol/L                      | 3.29E-05       | 1.31E-07     |                       |               |              |            |
| 42 |    | Sulfate, mg/L                      | 0.00           |              | 48.04                 |               | 0.000        |            |
| 43 |    | Chloride, mg/L                     | 7.00           |              | 35.45                 |               | 0.197        |            |
| 44 |    | Nitrate, mg/L                      | 25.96          |              | 62.00                 |               | 0.419        |            |
| 45 |    | Nitrite, mg/L                      | 0.0000         |              | 47.00                 |               | 0.000        |            |
| 46 |    | Sodium, mg/L                       | 9.6200         |              | 22.99                 | 0.418         |              |            |
| 47 |    | Potassium, mg/L                    | 1.00           |              | 39.10                 | 0.026         |              |            |
| 48 |    | Fe(II), mg/L                       | 0.00           |              | 27.92                 | 0.000         |              |            |
| 49 |    | Fe(III), mg/L                      | 0.00           |              | 18.62                 | 0.000         |              |            |
| 50 |    | Copper(II)mg/L                     | 0.00           |              | 31.77                 | 0.000         |              |            |
| 51 |    |                                    |                |              |                       |               |              |            |
| 52 |    | Free Ammonia, mg/L                 | 0.00           |              | 32.01                 | 0.000         |              |            |
| 53 |    |                                    |                |              |                       |               |              |            |
| 54 |    |                                    |                |              |                       |               |              |            |
| 55 |    |                                    |                |              |                       |               |              |            |
| 56 |    |                                    |                |              |                       |               |              |            |
| 57 |    |                                    |                |              |                       |               |              |            |
| 58 |    |                                    |                |              | <b>Charges, mEq/L</b> | <b>1.272</b>  | <b>1.272</b> |            |
| 59 |    |                                    |                |              | <b>Imbal., mEq/L</b>  | <b>0.000</b>  |              |            |
| 60 |    |                                    |                |              | <b>Imbal %</b>        | <b>0.00%</b>  |              |            |
| 61 |    | Alkalinity, mEq/L                  | 0.7000         |              |                       |               |              |            |
| 62 |    | Alkalinity, as CaCO3               | 35.00          |              |                       |               |              |            |
| 63 |    | Ca Hardness, as CaCO3              | 24.95          |              |                       |               |              |            |
| 64 |    | Mg Hardness, as CaCO3              | 16.46          |              |                       |               |              |            |
| 65 |    | Temporary Hardness                 | 35.00          |              |                       |               |              |            |
| 66 |    | Total Hardness, as CaCO3           | 41.41          |              |                       |               |              |            |
| 67 |    | Effective Hardness, as CaCO3       | 33.18          |              |                       |               |              |            |
| 68 |    | Residual Alkalinity                | 25.52          | ppm as CaCO3 |                       |               |              |            |
| 69 |    | Residual Alkalinity                | 0.51           | mEq/L        |                       |               |              |            |
| 70 |    | pH Shift RE Distilled Water        | 0.04           |              |                       |               |              |            |
| 71 |    | Stability                          |                |              |                       |               |              |            |
| 72 |    | pHs (CaCO3 Saturation pH)          | 8.81           |              |                       |               |              |            |
| 73 |    | SI = pH - pHs (Sat. Index)         | -2.11          |              |                       |               |              |            |
| 74 |    | CaCO3: Undersaturated by           | 2.1062         |              |                       |               |              |            |
| 75 |    | <b>Pa CO2, atm (Equil: 0.0003)</b> | <b>0.00766</b> |              |                       |               |              |            |
| 76 |    | Lime treatment trial Ca(OH)2       | 48.24          | mg/L         |                       |               |              |            |
| 77 |    | CO2 Vols. @ STP (0°C, 1 atm)       | 0.0067         |              |                       |               |              |            |

Screenshot 2. Example Source Artificially Balanced

## Target Water Area

(AB:AI,6:77) is the Target Water area of the spreadsheet. It is identical to the Source Water area in every way, with two minor exceptions. First, there is no choice available

with respect to the ideal or non-ideal model. Cell C7 in the Source Water portion of the spreadsheet is copied into Cell AD7 and sets the model for the entire spreadsheet. Second, the pH value in the Target Water area Cell AD8 represents the pH of the desired water. As such it is this pH that is used by the Synthesis portion of the spreadsheet for all its calculations *and it must be set to the proper value whenever the Synthesis portion is being used.*

Whereas the Source area describes the water you have the Target area describes the water you would like to have. Often this is the water reported as being found in a region where a style of beer you would like to brew originated. Burton on Trent is a common example and one we will use throughout. In entering a Target profile you must keep the same considerations in mind as when entering Source water data. In particular you must know the pH of the target water and the pH that defines its alkalinity. The profiles brewers use often come from brewing texts, magazine articles or the Internet. These sources seem to seldom, if ever, give pH information, and so you are immediately at somewhat of a disadvantage. A larger problem is that while these profiles often include “bicarbonate” or “carbonate” data, no one seems to know exactly what these numbers mean nor, indeed, is there any reason to suppose, given the time and geographical diversity over which these profiles have been collected, that there should even be consistency. Some theorize that these numbers are the total carbo, some that they are bicarbonate as the ion and some that they are alkalinity. If the data are accurate we should be able to discover which of the several possibilities the “bicarbonate” number represents by trying each possibility and selecting the one that balances electrically at a reasonable pH. Often this cannot be done. In fact no artifice will balance most of the profiles we have seen. Nevertheless, you must have a balanced target if you have any hope of achieving a reasonable synthesis. What this usually means is that in many, if not most, cases you will have to build a balanced profile that resembles what you have seen published rather than duplicating a particular profile.

In order to give some insight into how this might be done, we consider two profiles we have seen for Burton on Trent

|                            | <b>Profile 1</b> | <b>As Adjusted</b> | <b>Profile 2</b> | <b>As Adjusted</b> |
|----------------------------|------------------|--------------------|------------------|--------------------|
| <b>pH</b>                  | -                | 7                  | -                | 8.3                |
| <b>Calcium</b>             | 352              | 352                | 268              | 268                |
| <b>Magnesium</b>           | 24               | 24                 | 62               | 62                 |
| <b>“Bicarbonate”</b>       | 320              | 222                | 275              | 389                |
| <b>Sulfate</b>             | 820              | 820                | 638              | 638                |
| <b>Chloride</b>            | 16               | 16                 | 36               | 36                 |
| <b>Nitrate</b>             | 18               | 18                 | -                | -                  |
| <b>Sodium</b>              | 44               | 44                 | 54               | 54                 |
| <b>Residual Alkalinity</b> |                  | -78.2              |                  | 98.7               |

We begin with the first profile by entering all the numbers except the bicarbonate value into Col. AD in the Target Area, setting the pH to 7 in AD8 and end point pH to 4.3 (AE8). Note that it doesn't matter what value we put in for end point pH, as we are going

to vary carbo and the spreadsheet will calculate the alkalinity for that amount of carbo using the specified end point. This is in direct contrast with the case where alkalinity is specified and the amount of carbo must be calculated from it, which requires the end point pH to be known.

Put the Target Area into Carbo mode by entering 'C' in AB26. Temperature should be set to 20°C as it is for all examples in these instructions. Put some nominal value for total carbo such as 2 mMol/L into AD26 and note that the resulting imbalance is a relatively small 5%. This is because the calcium and sulfate ions swamp the others. Burton water is gypseous!

Next we ask the Solver to find the amount of carbo that will bring the water to neutrality, i.e. we ask it to zero cell AE54 by varying cell AB21 or we manually try values in cell AB21 until AE54 gets close to 0. After invoking the Solver, the Target Area of the spreadsheet should look like Screenshot 3 below. The Solver should find 4.37 mmol/L. This much carbo at pH 7 results in 221.95 mg/L bicarbonate and 45.4 mg/L carbonic. The sum of these is 267 mg/L, which isn't that far from 320 mg/L but isn't that close to it either. On the other hand, in this case we are pretty sure that 320 actually means bicarbonate because we have seen that number specifically labeled as bicarbonate ion concentration and attributed to Burton water in more than one source. Note that the residual alkalinity (AB63) would be -82.1, which is in the right arena (see Fig.1).

As a next step we might repeat the process describe above at a higher pH, say 7.2. Doing so results in a bicarbonate concentration of 221.76 mg/L – a little less than at pH 7. So let's try pH 6.6, at which we find the bicarbonate concentration to be 222.16 mg/L. So we have moved in the right direction but not far enough to make an appreciable difference in bicarbonate matching to the published profile. However, the total carbo is 5.48 mmol/L instead of 4.37, proportionally more of which is in the form of carbonic i.e. the lower the pH the more carbonic there will be in the water (72.0 mg/L at pH 6.8 as opposed to 45.4 mg/L at pH 7). As this carbonic comes from  $CO_2$  supplied by you when you synthesize this water, you might as well minimize the amount used. Furthermore, water with less  $CO_2$  (higher pH) is more stable as you can see by looking at Cell AD75 for all three trial pH's.

So let's go back to pH 7 and accept that the reported amount of bicarbonate simply isn't consistent with the amounts of other ions in the report. We note that this is the case with many, if not the majority of, the profiles we have seen. So we advocate the approach outlined above in which we determine how much bicarbonate is consistent, at reasonable pH, with the other ion concentrations. As noted above, at pH 7 the residual alkalinity is -82.1 ppm as  $CaCO_3$ . The end result is hard, gypseous water with a healthy negative RA. This is characteristic of Burton water.

If we now turn our attention to the second Burton profile in the table and take the same approach of seeing what level of bicarbonate gives balance for various pH levels, we find that the higher we go in pH the more closely the calculated bicarbonate matches the level in the profile. In fact if we impose upon the Solver the constraint that the bicarbonate

level in AD38 be 275 mg/L, as given in the profile, and allow it to vary carbo (AA21) and pH (AD8) to bring the imbalance (AG54) to zero, it is able to do that at pH 9.59. This is, by today's standards anyway, an unreasonably high pH. WHO recommendations limiting potable water pH to 8.3, but it is possible that at some time in the past a Burton well may have produced water like this. It would have an RA of 99 ppm as  $CaCO_3$ , however, and we don't think of Burton as having water with positive RA's.



the RA at 99 ppm as  $CaCO_3$  and results in a water well over saturated Cell AD74 with respect to  $CaCO_3$ .

If we set a reasonable pH such as 8.3, which is about as high as we want to go, we find balance when the bicarbonate level is 388.7, which is more than 100 mg/L more than in the profile, and the RA is 99 ppm as  $CaCO_3$ . We are forced to conclude that this particular profile is not a very good one and should choose another. We are not going to the trouble of synthesizing water for pale ale only to have it come up requiring treatment for high RA!

It is important to note that either of the adjusted profiles, even though the source data may have been erroneous, has been rendered physically realizable by our manipulations. You can synthesize either of the two example profiles we have looked at. The main concept that we wish to convey here is that you must be judicious in the choice of profile you chose for a target. After adjustment for realizability the profile must have the brewing properties you desire. The Target Area part of the NUBWS summarizes the target water properties in (AD,61:77) at the bottom.

## **Dilution Water Area**

The Dilution Water area is identical to the Source Water and Target Water areas, and as such all considerations pertaining to the use of those areas pertain here as well. There is no option to choose the ideal or non-ideal model, this having been set in the Source Water area. The main use of the Dilution Water area is to calculate the concentrations of carbonate, bicarbonate and carbonate in Dilution water and to pass these, along with other Dilution water concentrations that are entered directly (sulfate, chloride, sodium, etc.), to the Synthesis area, where they are multiplied by the dilution factor (Cell N22) and added to the ion concentrations from the Source water and ion concentrations caused by salts and acid additions (Row 27). The dilution factor is the number of liters of dilution water added to each liter of Source water. The salt additions in the Synthesis area are also per liter of source water. The total salts are divided by 1 plus the dilution factor, so that the *results, displayed in Col. W, are per liter of diluted water.*

The Dilution Water area can be used as a scratch area for storing or playing with water parameters. If you use it in this way be sure that the dilution factor in N27 is set to 0.

The dilution area can also be used as a “scratch” area for doing “what ifs”, saving a set of water parameters or anything you like.

## **Synthesis Area**

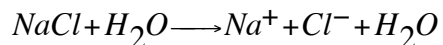
The Synthesis Area is located in the center of the spreadsheet. Here you enter amounts of salts, acids and/or dilution water in units of mg/L for all but the dilution water, which is entered in units of L/L. *The “per liter” part refers to liters of source water – not the final volume.* Thus, for example, if you intend to dilute your tap water to the extent of 2 L DI

water per liter of tap water, you would enter 2 in cell N27. If you specified 100 mg/L in cell K27 for a sodium chloride addition, that would mean that you want 100 mg per liter of the tap water, which, after addition of the dilution water is 100 mg per 3 liters or would 33.33 mg/L of the final, diluted water.

Dilution water is the only mechanism available for reducing the concentration of an ion and the limit to which an ion can be reduced is the concentration of that ion in the dilution water.

Ions from dissociation of the salt additions you specify are added to ions in the source water, and the sums displayed at the right side of the Synthesis Area in Col. Z. Thus if we specify a Source water with calcium hardness of 100 ppm as  $CaCO_3$  (2 mEq/L or 40 mg/L or 1 mmol/L) and chloride content of 70.90 (2 mmol/L – atomic weight of chloride is 35.45 g/mol), and then specify an addition of a mole of calcium chloride dihydrate that weighs 147.02 g/mol (as shown in cell J28) by entering 147.02 in cell J27, it should be no surprise that the calcium level displayed in W30 is 80 mg/L (twice what is in A38) nor that the chloride level in W43 it also twice what it was in the source at C43.

The simple summation of ions that takes place with sodium chloride also happens with other salts of strong acids and weak bases such as calcium chloride, magnesium sulfate and calcium sulfate (gypsum), but only with those salts. For any of the acids or other salts, and to a lesser extent with dilution water, things get more complicated. This is because the four salts of Col. J:N simply split into their constituent ions, e.g.



whatever the pH. Note that when you enter an amount of one of these salts the amount of each ion, in moles/L, appears in the column for that salt. For example, if you enter 246.47 mg/L in N27 (magnesium sulfate), a 1 appears in N31 (the row for magnesium) and another 1 in N42 (the row for sulfate). This is because the gram molecular weight of magnesium sulfate heptahydrate (displayed in N28) is 246.47, and thus 1 mmol/L of each ion has been added to the Source Water.

A salt like sodium bicarbonate acts differently when added to water and what happens depends on the pH. This is why consideration of pH is, as we noted in the Introduction, so important. Carbo (recall that this is the collective term for carbonic, bicarbonate and carbonate) is distributed according to pH. In calculating the distribution of carbo added in the Synthesis area the Target Water pH (AD8) is used because this is the pH the addition will experience when the water is synthesized. In sodium bicarbonate all the carbo is, obviously, in the form of bicarbonate. In water the carbo is never 100% bicarbonate. Even at pH 8.38, the pH at which bicarbonate concentration is maximum, only 98% of a bicarbonate addition remains bicarbonate with about 1% taking up protons to become carbonic acid molecules and another 1% shedding protons to become carbonate ions.

When an addition of a salt like sodium bicarbonate is specified, the spreadsheet first uses the Target Area pH to calculate the carbo ion species distribution fractions (see Appendix

B for an explanation of how these are calculated) for that pH. These are displayed in (AD,20:23), and, if non-ideal chemistry has been selected, more precisely in (J,140:142). Next it multiplies these fractions by the total carbo content of the addition to get the amounts of each of the 3 species from that addition. Next the protons required to effect the conversions from the form added to the new forms are tallied and this is added to the Proton Deficit (Z40). For example, if 84 mg/L (1 mmol/L) of sodium bicarbonate is added to a water which is to be at pH 7 where 19.4% of carbo is carbonic, 80.6% is bicarbonate and 0.03% is carbonate it is clear that .1940 mmol/L (mEq/L) of protons would be required to change bicarbonate to carbonic while .0003 mmol/L (mEq/L) would be given up when a very small amount of bicarbonate was converted to carbonate. Thus the Proton Deficit increment for this addition is  $0.1940 - 0.0003 = 0.1937$  mEq/L. The interpretation of this is that 0.1937 mEq/L of protons will have to be added to the water in addition to the 84 mg/L of bicarbonate if the pH is to be brought to 7<sup>6</sup>. This is done by adding some form of acid (hydrochloric, sulfuric, carbonic or one of the special acids) or an acid salt to the synthesis area until the Proton Deficit is 0.

Sodium and potassium bicarbonate, calcium carbonate, carbon dioxide, and special acids and salts are all treated in this way and contribute to the Proton Deficit. Distributions of special acid species are displayed in (J,148:151).

A positive Proton Deficit means that protons are needed to establish the requested pH and that acid must be added. A negative proton deficit in Z40 means that protons need to be absorbed and that a base should be added. To absorb protons we add base usually in the form of a basic salt. Calcium carbonate and sodium bicarbonate are the most commonly used salts but others such as sodium carbonate, dibasic sodium phosphate or tribasic potassium phosphate would also serve. We could, of course, use straight bases such as sodium, potassium or calcium hydroxide but as this is seldom done by brewers<sup>7</sup> the NUWBS does not have columns for these – it is big enough as it is. To supply protons we usually add an acid. Hydrochloric, sulfuric, phosphoric, lactic and carbonic are the most common but we could use an acid salt (monobasic sodium citrate, monobasic potassium phosphate, sodium bisulfate etc.).

*Cell Z40 (proton deficit) is one of the most important cells in the NUBWS. It tells you what you must do with regard to acid or base additions in order to set the pH in a synthesis to the value you have specified in the Target Area (Cell AD8). At this point we will continue the discussion through illustrative examples. You will see that in each case keeping the proton deficit at zero is essential.*

---

<sup>6</sup> If the addition is made to distilled water and no acid is added the pH will go to 8.38 for at this pH the number of protons yielded in conversion to carbonate just equals the number consumed by conversion to carbonic resulting in 0 proton deficit.

<sup>7</sup> Brewers do, of course, use lime (calcium hydroxide) for decarbonation of water but not usually to establish ion profiles. The more commonly used salts are adequate for this purpose.

Before moving on to some examples we note that one can specify either sodium bicarbonate or potassium bicarbonate in Column Q. The choice is made by entering either Na or K into Q24. Those with potassium bicarbonate available (sold by wine making supply shops) might wish to use this salt to increase alkalinity without increasing the sodium load.

**Example 1:** You have the water of Screenshot 1 and have modified its profile to balance per Screenshot 2. You want really soft water so you dilute 1 part of the source water with 4 parts of deionized water. What does the water look like now?

Fill in the Screenshot 2 data in the Source Area, and then check that all cells in (J:Y, 27) contain 0's. Now set the target pH in AD7 to 6.7. Check that the proton deficit in Z40 is 0. Go to the Dilution Water area. Enter 7 for the pH in AQ8, 'C' in AO26 and 0 in AQ6, Check that all entries in (AQ,42:52) are 0. Now enter 4 L/L in O27. Note that the proton deficit takes on the value 0.0011. This is telling you that when you add the dilution water you have diluted the hydrogen ions in the source to the point that they are insufficient to maintain pH 6.7. You would need to add some acid (source of protons) in order to hold pH 6.7, and Cell Z41 instructs you to do exactly that.

The proton deficit is a consequence of your having instructed the Synthesis to do calculations based on a pH of 6.7 in the target water. If you don't care about maintaining this pH, simply adjust the Target Water pH until W35 returns to 0, which should happen at pH 6.712. The protons in 1 L of the source water are sufficient to maintain pH 6.712 when it is diluted to 5 L with DI water. This is a very small shift, in fact negligible, so that you wouldn't even think about adding the extra acid to maintain pH 6.7. Were you to do so, however, you would set the Target pH back to 6.7 and then enter tiny amounts of the acid of your choice in Row 27 until the proton deficit was returned to 0. The proton deficit could be covered by 0.36 mg/L  $CO_2$  or 0.50 mg/L lactic acid. To calculate lactic set X24 to 2 and then specify small amounts in X27. If you put the original volume of water to be treated, say 5 gallons, in J75 the spreadsheet will display the fact that 0.01 mL of 88% acid is needed in X79. Just to be clear this is the amount of acid that will be added to the blend (e.g. 25 gallons in this case made up of the original 5 gallons plus the 30 gallons dilution water).

Assume that you do not add acid (set the acid addition back to 0 and the Target pH back to 6.712 if you changed it, and look at the summary data at the bottom of the Synthesis Area in Col. Z). Note that most ion concentrations and parameters related to them alone, such as hardnesses, drop by a factor of five as you might expect. Alkalinity and parameters derived from it, such as temporary hardness and Residual Alkalinity, change by an amount that is a little less than a factor of 5. The diluted water is seen to be less oversaturated with respect to  $CO_2$  than the original.

**Example 2:** You have the water of Screenshot 1 and have modified its profile to balance per Screenshot 2. You would like to lower the pH of this water to 5.8 for sparging and want to know how much acid to add.

Start by setting the Screenshot numbers into the Source Water area. Copy the total carbo from C36 into C26 and set A26 to 'C'. Now enter 5.8 into D8. C61 shows that the alkalinity to endpoint 5.8, which is the amount of acid required to bring the sample to that pH, is 0.4521 mEq/L. Restore D7 to 4.3.

Check that all cells in (J:X,27) are set to 0 and then enter pH 5.8 into AD8 in the Target Area. Cell Z40 shows that you must add 0.4521 mEq/L of acid to effect this pH reduction, and Cell Z41 instructs you to add either acid or CO<sub>2</sub>. Trying values in R27, you will quickly find that 95.71 mg/L CO<sub>2</sub> will zero the proton deficit and thus accomplish the pH reduction. But a look at (Y:Z,75) shows that the water will be supersaturated with CO<sub>2</sub> to the extent of 0.06 atmospheres and the gas would certainly escape when the water is heated to sparge temperature. Carbonic acid is not the acid to use here. So set R27 to 0 and try some numbers in S27 for hydrochloric acid. You should pretty quickly discover that 16.47 mg/L hydrochloric acid will do the job and it will not be driven off by heat. Enter the volume of water to be treated in Cell J70 as a positive number if expressed in gallons or a negative number if in liters. Using 5 gallons as an example, type in 5. Cell J71 converts this to 18.927 liters for you and Cell R74 shows you that a total of 0.69 mL of 23 Baume acid would be required to treat the 5 gallons.

Lactic acid is a popular choice for this job and will allow us to illustrate the use of "special" acids. Set S27 to 0 and enter a 2 in Cell X27. This will cause lactate labels to appear in Cols. V and W (and lactic labels elsewhere), but these are not, for the moment, of concern, as we will be using lactic acid and Cols V and W deal with the salts of acids. Again it should take but a few trial entries in Cell X27 to discover that 41.13 mg of lactic acid are required to cover the proton deficit for each liter of this water. Cell X79 reports that 0.73 mL of 88% acid (the most common strength) are sufficient to treat 5 gallons. Should the acid you have be of a different strength, you must enter the strength, as a percent, in Cell Y87 and the density of the solution in Z87.

Salts of strong acids can also supply protons. The special salts portion of the NUBWS is located in Cols. V and W and the data on the special salts in (N:Z, 85:106). The table there is pre-loaded with data on citric, lactic, phosphoric and tartaric acids. There is room for two more acids and we have entered data for sulfuric acid in one of them mostly to illustrate how this is done. Under pK1 for sulfuric we have entered -3, which is one published value for the first pK of sulfuric acid we have seen. Any negative number will do as the software will release 100% of first protons (or very, very close to it) for any pH you will encounter using this spreadsheet when the first pK is negative. For pK2 we have entered 1.92, which is the accepted value for the second proton of sulfuric acid. For pK3 the value 40 is entered. In response to a pK this high the spreadsheet calculates the production of effectively 0 third protons, which is correct, as sulfuric acid doesn't have a third proton (though the mathematics aren't aware of this). In the Mol. Wt. Column we

have entered 98, the gram molecular weight of sulfuric acid and in X85 the density of 98% sulfuric acid which is 1.856 g/cc<sup>8</sup>.

Columns V and W contain information about the sodium or potassium salts of the special acid selected in Cell X24. If a 1 has been entered in Cell V21, then Col. V will be for a monobasic salt of the acid, e.g.  $\text{NaH}_2\text{PO}_4$  and Col. W will be for the dibasic salt, e.g.  $\text{Na}_2\text{HPO}_4$ . If Cell V21 contains a 2, then Col. V is for the dibasic salt and Col. W for the tribasic, e.g.  $\text{Na}_3\text{PO}_4$ . Things are done this way to allow you to design buffers (salt or acid salt mixtures that try to hold a given pH value). It would be unusual for us as brewers to work with buffers involving a tribasic salt, so V21 will nearly always be set to 1.

In (V:W,24) you enter either K, for the potassium salt, or Na for the sodium. Actually, anything other than K will cause the spreadsheet to conclude you want to use sodium salts. Cells (V:W,25,26) then contain labels with the name of the salt, which depends on your entries in V21, (V:W,24) and X24. For example, if you set X24 to 5 (and sulfuric acid data is still in (O:Z,90)), V21 to 1, V24 to Na and W24 to K, you will see the label “mg Monobasic Sodium Sulfate” in (V, 25:26) and “mg Dibasic Potassium Sulfate” in (W, 25:26). Monobasic Sodium Sulfate,  $\text{NaHSO}_4$ , is usually called *sodium bisulfate*, and dibasic potassium sulfate is  $\text{K}_2\text{SO}_4$ , is usually just called *sodium sulfate*. In other words the NUBWS is more formal than usual and is so in order to accommodate a wide range of salts.

In (V:W,29) you will see either TRUE or FALSE. TRUE means the salt can exist, and if TRUE appears below it will appear the message “This Salt Exists”. Existence here simply means that there are no more sodium or potassium ions in the named salt than there were hydrogen ions in the un-dissociated acid.  $\text{NaHSO}_4$  and  $\text{K}_2\text{SO}_4$  both satisfy this rule so TRUE appears when their names appear..

If you now change V21 to 2, the labels change to “mg Dibasic Sodium Sulfate” and “mg Tribasic Potassium Sulfate”. As there is no such thing as the latter ( $\text{K}_3\text{SO}_4$ ) because sulfuric acid doesn't have 3 protons that can be replaced by potassium, FALSE is displayed in W29 and “This Salt Doesn't Exist” appears in W30. Beyond this proton check the NUBWS doesn't know anything further about the existence or nonexistence of a salt. Even though bizzaric (made-up name) acid may carry 3 or more protons, the trisodium salt may or may not exist.

Before moving on we should note that the ability to play “what if” with additions will as we have done here will prove to to be where the true value of the NUBWS lies. Not only

---

<sup>8</sup> If you enter sulfuric acid in Y27 each molecule will be assumed to release 2 protons whatever the pH. If the pH in AD8 is less than 2 units above this (3.92) you should not use Col. Y for sulfuric acid but instead enter the given sulfuric acid parameters in one of the blank slots (N:Z,90:91) in the special acids table, select the appropriate number (5 or 6) in X24 and specify the addition amount in X27.

can this ability be used to arrive at solutions to problems but we believe it will be of great value in getting to the point where users actually get a feel for what brewing chemistry is really about.

**Example 3:** You have the water of Screenshot 1 and have tweaked its parameters to give the balanced results in Screenshot 2. You have a nearby friend with a very soft well whose water has a pH of 7.2, alkalinity of 10, calcium hardness of 8, magnesium hardness of 0 (all ppm as  $CaCO_3$ ), chloride of 3.5 mg/L and sodium at 2 mg/L, which is a well balanced profile. What happens if you dilute your water with his in the ratio 1:1, 1:2, 1:3?

Enter the Screenshot 2 data into the Source area and set Target pH in AD7 to match the source pH of 6.7. Enter your friend's specs into the Dilution Water area. Set all cells in Row 27 in the Synthesis area to 0. Check that the imbalance is Z40 is 0 and that all the parameters in Col. Z match those of the Source that are listed in the table below in the column labeled "Source (1:0)". Now set the Dilution factor in O27 to 1. The imbalance shows 0.0174 mEq/L proton deficit with the instruction to add acid. We don't want to add anything here but rather see what the pH would be if we prepared this 1:1 blend. So we adjust the target pH in AD8 until W35 is 0 or very close to it. If W36 says to add acid, we know that we should raise the pH (i.e. establish a pH in which fewer protons are needed). Trial and error shows that a pH of 6.763 will balance the protons. This is the pH to which the blend will come.

Read the other parameters from Col. W. They are listed in the table below in the column labeled 1:1. Other data in this table show what happens when dilutions of 1:2, 1:3, 1:10 are made and the parameters for the dilution water as taken from the Dilution Water area (column labeled "Dil. 0:1"). The parameters of the source water are summarized in the column labeled "Source 1:0".

| Parameter   | Source 1:0 | 1:1   | 1:2   | 1:3   | 1:10  | Dil. 0:1 |
|-------------|------------|-------|-------|-------|-------|----------|
| pH          | 6.70       | 6.763 | 6.876 | 6.971 | 7.162 | 7.2      |
| Alkalinity  | 35         | 22.51 | 18.96 | 17.17 | 12.96 | 10       |
| Ca Hardness | 24.95      | 16.48 | 13.65 | 12.24 | 9.54  | 8        |
| Mg Hardness | 16.46      | 8.23  | 5.49  | 4.11  | 1.5   | 0        |
| Chloride    | 7          | 5.25  | 4.7   | 4.37  | 3.82  | 3.5      |
| Sodium      | 9.62       | 5.81  | 4.54  | 3.9   | 2.70  | 2        |
| Nitrate     | 25.96      | 12.98 | 8.65  | 6.5   | 2.36  | 0        |
| Total Hard. | 41.41      | 24.7  | 19.14 | 16.35 | 11    | 8        |
| Res. Alk.   | 25.52      | 16.58 | 14.3  | 13.1  | 10.0  | 7.7      |

You will note that for an n:m dilution the ion concentration is n times the concentration in the source water plus m times the concentration in the dilution water divided by n+m, This rule is followed closely by all the ions but not by the alkalinity values though they follow it approximately. For 1:1 dilution the rule would give 22.5 whereas the spreadsheet calculated 22.51 with the difference being caused by the pH shift. Where the

pH shift is larger the departure from the rule is larger. For 1:3 dilution the rule gives alkalinity of 16.25 whereas the spreadsheet calculates 17.17.

**Example 4:** You have the water of Screenshot 1 available and have adjusted its profile to that of Screenshot 2. You want to brew a Burton style pale ale. You consult Figure 1 and see that the Burton waters all have very high effective hardnesses – around 800 ppm as  $CaCO_3$ . You have heard that magnesium is bitter and can cause diarrhea so you decide to limit the amount of magnesium you will allow to 20 mg/L (magnesium hardness of 82.3 ppm as  $CaCO_3$ ). You decide that pH 7.4 is a reasonable value for the synthesized water and you decide you want to imitate nature by using carbonic acid to dissolve any  $CaCO_3$  that you may need to use.

You start, as in the other examples, by entering the data from Screenshot 2 into the Source Water area. You set pH 6.7 into Cell AD8 in the Target Water area for now (it will be changed to 7.4 later) and zero all the salt and acid inputs in the Synthesis area Row 27. You know you are going to want no more than 20 mg/L magnesium, so you start adding Epsom salts in N27 until you get something close to 20 mg/L in Cell Z31 (which is initially at 4 mg/L from the Source Water). An entry of 200 mg/L Epsom salts gives 23.72 mg/L  $Mg^{+2}$ , but just leave that for now as you are shooting for a rough solution at this point which solution we will have the Solver refine. You may have noted that (Z,40:41) have turned red telling you to add base. Rather than doing that tweak the target pH in AD3 until Z40 is 0. This will happen near pH 6.6873. What this tells you is that if you take water with dissociated acid in it (carbonic acid with bicarbonate and carbonate here) and add a fair amount of a neutral salt to it the pH will decline slightly. This is the effect of the magnesium and sulfate ions on the dissociation constants of the carbonic acid. Put the pH back to 6.7 for the following parts of this example.

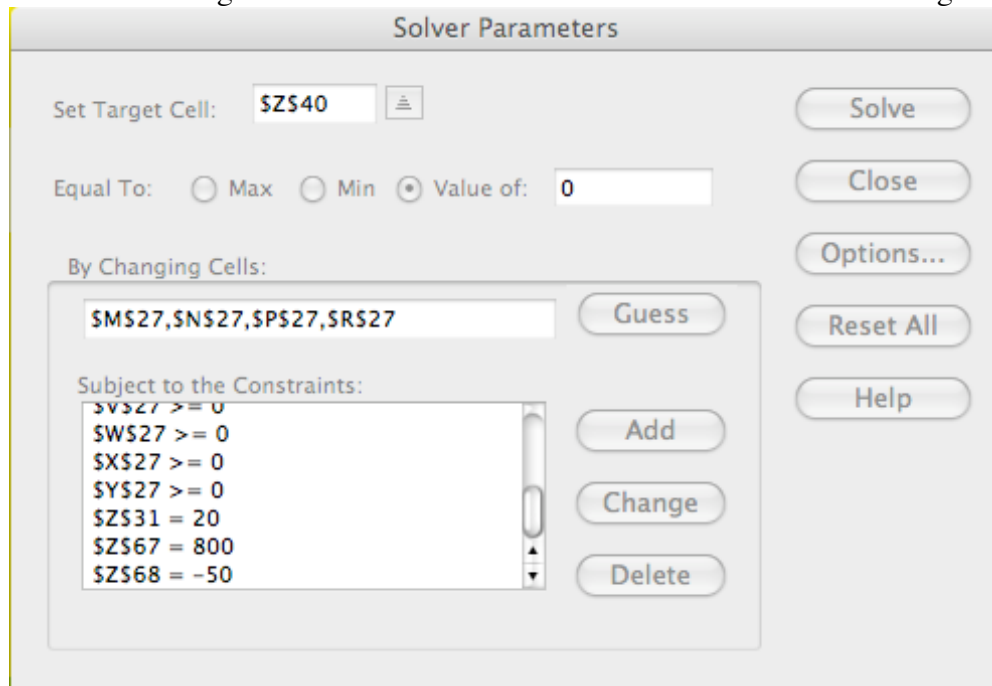
Observe that the effective hardness (Z67) is 73.75 at this point so you are, given that you have all the  $Mg^{+2}$  you have chosen to allow, going to need lots of  $Ca^{+2}$  which, for Burton water, is mostly in the form of gypsum ( $CaSO_4$ ). Start entering gypsum increments in M27 while watching the effective hardness in Z67. An entry of 1200 mg/L gives an effective hardness of 770.7, which is pretty close to the goal of 800. Now a check of the residual alkalinity (Z68) shows that it is, at -184, way lower than what is typical for Burton. As you can still add some calcium without exceeding the desired effective hardness and as carbonate is 7 times more effective at increasing alkalinity than calcium is in lowering it<sup>9</sup>, you can increase RA by adding  $CaCO_3$  in P27. Alkalinity is, at this point, only 36 ppm as  $CaCO_3$  and this derives from the Source Water. So let's add 100 mg/L in O27 and see what happens. Alkalinity approximately doubles but RA only increases to -177 but these numbers must, for the moment be disregarded as Z40 shows a large proton imbalance which, according to Z41 can be repaired by adding acid. This acid

---

<sup>9</sup> This may at first appear to conflict with Kolbach's observation that each 3.5 mEq of calcium neutralize 1 of alkalinity but it doesn't because a carbonate ion has first to be converted to bicarbonate and then to carbonic so that its alkalinity is twice that of a bicarbonate ion.

will convert the carbonate ions from the added  $\text{CaCO}_3$  to bicarbonate and carbonic (cells AD20 and AD21 show that, respectively, 32% and 68% of carbo is, respectively, carbonic and bicarbonate at pH 6.7). You have decided to use  $\text{CO}_2$  as your acid source, so try additions of  $\text{CO}_2$  in R27 to get Z40 close to 0. Eighty five (85) mg gets you pretty close to zero, raises you alkalinity to 135 and your RA up to  $-109$  from which it is clear that the combination of  $\text{CO}_2$  and  $\text{CaCO}_3$  is a great way to increase alkalinity. To illustrate its effectiveness relative to other acids set R27 to 0 and enter 47.5 in S27 (hydrochloric acid). This also comes close to zeroing the proton deficit but results in an RA of  $-177$  and alkalinity of 72 which shows the value of making up proton deficit with carbonic in terms of effective alkalinity increase. Return R27 to 85 and S27 to 0 before continuing with this example.

Now that you have somewhat of an idea of what tweaking various salt additions does let us ask the Solver to give us a solution with the values specified in Screenshot 4 below. Note that we are asking Solver to set the Proton Balance to 0. This is something that we



Screenshot 4

will very often want it to do and so leaving the “Set Target Cell” field set this way is a convenient thing to do. Note that we are asking Solver to adjust gypsum (M27), Epsom salts (N,27), chalk (P27) and carbon dioxide (R27) to zero Proton Balance subject to the constraints that magnesium (Z31) be 20 mg/L, Effective Hardness (Z67) be 800 and the Residual Alkalinity (Z68) be  $-50$ . The other constraints which are not all visible are simply that any thing in (J:Y,27) i.e. anything in a cell into which a salt, water or acid addition can be made, be positive. This is, of course, a perfectly reasonable thing to do as there is no way in which we can subtract, for example, a gram of sodium chloride from distilled water. We note again that the spreadsheet only understands numbers and is perfectly happy to make calculations with negative ion concentrations if that will allow it

to get it closer to whatever goal we have set for it. Because there is no situation in which these constraints limit the performance of the spreadsheet we leave them set all the time.

The Solver is able to find a solution that meets all constraints. It calls for 1026 mg/L (yes, over a gram per liter) of  $CaSO_4 \cdot 2H_2O$ , 162.25 mg/L  $MgSO_4 \cdot 7H_2O$ , 138 mg/L  $CaCO_3$  and 117.47 mg/L  $CO_2$ . When this water is synthesized the salts will be added to it and suspended and then the  $CO_2$  will be sparged through to form the carbonic acid which will first dissolve the chalk, then convert carbonate ions to bicarbonate and some of them subsequently to carbonic molecules and set the pH. There is really no need to have the pH as low as in the source water as this will require extra  $CO_2$ . If we, therefore, set the target pH in AD8 to 7.4 (chosen more or less arbitrarily) and run the solver again we find that only 63.6 mg/L  $CO_2$  are required. Synthesizing at this higher pH will not only save us some money on  $CO_2$  but also some time as the  $CO_2$  reacts quite slowly. Note that at this higher pH the required  $CaSO_4 \cdot 2H_2O$  is a little less at 1018 mg/L and the required  $CaCO_3$  a little greater at 142.8 but that the  $MgSO_4 \cdot 7H_2O$  stays the same.

The results of the synthesis can be seen in Screenshot5 below. Note that we added some sodium chloride (45 mg/L) after application of the Solver to get some sodium and chloride ions into the mix as is typical of Burton water that there be some of these. Note also that this has caused a proton deficit of  $-0.0001$  even though the Solver had set the deficit to exactly 0. This insignificant deficit is a consequence of the non-ideal solution chemistry assumed here. It would not occur with the ideally dilute assumption.

The “wild card” in this synthesis was the sulfate. It was allowed to go wherever it wanted. As Screenshot3 shows, it wound up at 631 mg/L. This is certainly an acceptable level of sulfate and overall an acceptable synthesis for a Burton Style ale. The reason it is so is that you have done essentially what nature does in the Burton region, which is dissolve gypsum, ordinary table salt and limestone in water, using  $CO_2$  as the acid.

This is probably as reasonable a way to prepare a Burton water synthesis as any given the problems with profiles discussed in the section Target Water Area above. Nonetheless we will soon have an example of how to synthesize Burton water from a profile. This will be found in the section on Synthesis Quality.

---



synthesized water pH is only 7.4. If this water is subjected to heating such as in the mash tun or HLT, it will become well oversaturated with respect to  $CaCO_3$  and chalk will precipitate. This will happen to you if you synthesize this water, and it will happen to a brewer in Burton using the water after which this water is modeled.

The equilibrium partial pressure of  $CO_2$  in this synthesis is almost 21 times the partial pressure of  $CO_2$  in the atmosphere. This water will, therefore, over time lose  $CO_2$  and its pH will rise.

## Synthesis-Target Comparison Area

In the preceding section we discussed how to synthesize a Burton-like water based on general knowledge of what Burton water is like. In this section we will discuss the related problem of determining what salts and acids to add to duplicate, as closely as possible, a given water ion profile. That profile is specified in the Target Water area, and in the section devoted to that part of the NUBWS we discussed the problems with reported profiles and what to do about them. In the material presented in this section we assume that the user has a Target profile that is balanced and with which he is satisfied.

Clearly the basic approach to synthesizing a given profile is to compare the results of a synthesis as given in Col. Z with desired ion concentrations which have been entered in Col. AD and this is the function of the Synthesis Quality area located between the Target and Dilution water areas. It might seem obvious that the way to do this is to take the difference between, say, the mg/L calcium in the synthesis and the mg/L in the desired profile. The problem with doing this is that in Burton water, for example, the error incurred by neglecting to supply any chloride at all might amount to some 30 mg/L. With respect to the sulfate in such water, a 30 mg/L error would only amount to 5%. It seems more reasonable therefore to specify errors in terms of the ratios of the desired and achieved ion concentrations in other words to compute errors on a geometric rather than arithmetic basis. Ratios are very conveniently manipulated by use of the logarithm, and as we are using the  $p$  operator elsewhere we will define the error for an ion  $i$  as  $\epsilon_i = p(\text{realized\_concentration}) - p(\text{desired\_concentration})$ <sup>11</sup>. We are interested in a number that describes the overall “goodness” of the synthesis. The *root mean square* error has several desirable properties and we have chosen it for this reason. The overall error is

---

<sup>11</sup> A difficulty with this approach arises if the concentration of an ion in either the synthesis or the target is 0. Computers do not like being asked to take the logarithm of 0 as it is minus infinity. To work around this problem we add a tiny number to each concentration so that log of 0 is never requested. This can still lead to percentage errors in Col AL so large that they can't be displayed in which case ##### appears. Obviously small weights (see text below) should be applied to ions for which no target concentration has been specified or which are absent from the synthesis.

$$E = \sqrt{\frac{1}{N} \sum_{i=1}^N w_i \varepsilon_i^2}$$

where we have added the factors  $w_i$  as “weights” for the individual ions. Thus if we want all ions to be considered equally in computing the overall error, we set all the weights to the same value, usually 1 or 100. The main reason for doing this is that when the Solver is used to determine the amounts of salt and acid additions it will be set to minimize this weighted RMSE. If we wished, for example, to get the bicarbonate quite close to a particular value but didn’t care that much about where the sulfate wound up, we would assign a large weight (say 100) to bicarbonate and a low one (say 1) to sulfate. If we care about both but want the bicarbonate better controlled, we would set its weight to say, 100, and the sulfate’s weight to perhaps 50. The weights are entered in Col. AK and the value used for  $N$  is the number of these that are non-zero. In other words, if the user deems a particular ion’s concentration error not important, he weights it with 0 and its error is then neither included in the sum nor does the average include it. The calculated weighted RMSE appears in AH49. The significance of the RMSE is seen when we ask the Solver to minimize it by varying salt and acid additions in the Synthesis section. Engineers often refer to solutions found this way as Minimum Mean Square Error (MMSE) solutions<sup>12</sup>.

The actual errors in mg/L are shown in Col AM and the errors as percentages of the desired ion concentration in Col AL. Thus, for example, if the Target Water profile specifies a desired 40 mg/L magnesium and the synthesis gives 20, the error is  $-20$  mg/L, which as a percentage of the desired amount is  $-50\%$ . The percentage errors can also be inserted into the RMSE formula above, and the NUBWS puts the resulting value in Cell AL54. The weights are applied in the same manner.

Note that the percent-based RMSE is not an ordinary average. For example, if we only cared about 2 ions (only 2 non-zero weights) and one of them exhibited 50% error while the other exhibited  $-50\%$ , the opposite signs would not cancel and the RMSE % would *not* be 0 but rather 50% because each of the errors was of this *magnitude* though of opposite sign. The RMSE % will always be a positive number.

The Solver can also be set to minimize the percentage-based RMSE and should give the same solution, whichever is chosen, as minimizing the p-based RMSE will also minimize the percentage-based RMSE. Peculiarities of the Solver algorithms may, in some cases, result in slightly different answers.

**Example 5:** A brewer has the water of Screenshot 1, has adjusted the profile to that of Screenshot 2 and wishes to emulate Burton water as represented by Screenshot 3, which is a published profile modified to be physically realizable. He decides to shoot for neutral pH 7.

---

<sup>12</sup> If the RMSE is minimized so is the Mean Square Error as they are monotonic functions of each other. MMSE is just easier to say.

To compute the salt additions start by copying the Screenshot 2 data into the Source Water Area and the Screenshot 3 data into the Target Water Area. Set target water pH to 7. In the Synthesis Quality area set the weights (Col. AK) to 1 for all ions except Nitrate, Nitrite, Potassium, Fe(II), Fe(III) and Ammonium as none of these ions are listed in the target profile and even if they were you could only adjust potassium through addition of potassium chloride. Thus there is no point in including them in the computed error. Now set all salt and acid addition values to 0 in Row 27 in the Synthesis area.

Examine Col. X, AB and AK. From these you can see that you need to add a lot of calcium, bicarbonate and sulfate, and more modest amounts of sodium and magnesium. As you are most shy on sulfate, start with gypsum additions in 100 mg/L increments in Cell M22. You will find that it takes 1450 mg/L  $CaSO_4 \cdot 2H_2O$  to get the sulfate deficit down to around 11, which simultaneously raises the calcium too high by 3.6 mg/L. Leave 1450 in Cell M22. We are, at this point, just trying to get into range where the Solver can take over. You see now that you are shy on magnesium and chloride both, so try additions of  $MgSO_4 \cdot 7H_2O$  in Cell N22 in 100 mg/L increments. You should find that 200 mg/L of this salt reduces the magnesium deficit to under 1 mg/L while pushing the sulfate over by 67. Don't worry about this now. Now add calcium carbonate (Cell P22) in 100 mg/L increments and find that 300 mg/L brings the bicarbonate to 21 mg/L over target but pushes the calcium well over (115.8 mg/L). So try dropping the gypsum (M22) in 100 mg/L increments. An addition of 1250 mg/L brings the calcium down to 69 mg/L and the sulfate to 44.5 under. This splits the error about equally, so leave it for now.

We still haven't done anything about the sodium or chloride, so add some sodium chloride in K22. A value of 20 mg/L gets the chloride about where it needs to be but leaves the sodium shy. So try adding some sodium bicarbonate (Cell Q22). One hundred (100) mg/L of this causes overshoot of the bicarbonate by 39.7 mg/L but brings the sodium shortfall to -7.

As soon as we added the calcium sulfate the proton deficit annunciator turned red, and when we added the carbonate and bicarbonate it shows us to be shy of acid by 3.7 mEq/L. As we like, in general, to emulate nature and use  $CO_2$  for acid, start adding increments of this in R22. An addition of 200 mg/L knocks out the proton deficit but the bicarbonate is now way over at +271 mg/L. Reduce carbonate in increments and add enough  $CO_2$  to keep balanced as you do so. After some tweaking you will find that 100 mg/L calcium carbonate and 70 mg/L  $CO_2$  gives proton balance and leaves the bicarbonate over by only 18.6. This is close enough for the Solver.

Set the Solver to minimize the Weighted RMS error (Cell AH49) by adjusting J22, K22, M22, N22, P22, Q22 and R22 subject to the constraints that each of these is greater than or equal to 0 and that the proton deficit (Cell Z35) be equal to 0.

The solver should find a solution something like the values in the first column of the following table:

| Salt/Acid, mg/L    | Start CaCl <sub>2</sub> 0 mg/L | Start CaCl <sub>2</sub> 10 mg/L | Start w/ all salts & acids 0 | Col. 4 Sol. w/ wt of 10 on Ca & SO <sub>4</sub> |
|--------------------|--------------------------------|---------------------------------|------------------------------|---|
| Calcium Chloride   | 4.76                           | 6.30                            | 17.65                        | 10.29   |
| Sodium Chloride    | 11.06                          | 9.83                            | 0.68                         | 6.65  |
| Calcium Sulfate    | 1327.44                        | 1327.42                         | 1263.95                      | 1327.48   |
| Magnesium Sulfate  | 202.82                         | 202.82                          | 203.4                        | 202.88  |
| Calcium Carbonate  | 79.34                          | 78.29                           | 71.37                        | 75.48   |
| Sodium Bicarbonate | 109.76                         | 111.52                          | 124.54                       | 116.12  |
| Carbon Dioxide     | 57.76                          | 57.30                           | 54.45                        | 56.05   |
| Wtd RMSE, %        | 0.0181%                        | 0.0180%                         | 2.4%                         | 0.0501%   |

The solution you obtained should be close to this but not necessarily exactly the same. Try setting the calcium chloride addition in J22 to 10 and run the Solver again. You should get numbers close to what is in the third column in the table. Note the values found for the various salts will change but the RMSE (Cell AI49) will stay the same. This is because the solution is not unique. There are an infinite number of combinations of the various salts that will produce water with a profile that resembles the target water very closely.

Note that Cell AI49 contains a very small number and that the individual errors for the ions we varied (i.e. nitrate and potassium are excluded) are at the fraction of mg/L level. These are both excellent syntheses!

You may have concluded that the fumbling around manually to get a solution in range of the Solver is painful, or you may not, at first, have the experience to be able to do the manual searching confidently. What, you may wonder, would happen if we just threw the problem at the Solver with all the initial inputs set to 0? The solution found in this case should be close to that of the 4<sup>th</sup> column of the table. You will note that the Solver takes much longer to find the solution and that the solution is not nearly as good as the solutions found after trying to set up the problem to the Solver's liking. The weighted RMSE (in %) is 2.4% - orders of magnitude higher than for the tailored solutions. An examination of the individual ion errors shows that calcium is under the target by 4.1% and sulfate under by 4.3%, whereas all errors were a fraction of a percent in the tailored solutions.

Given this we could try to fix the problem by raising the weight on calcium and sulfate errors while leaving all the other weights set to 1. Using a value of 10 for calcium and sulfate and rerunning the Solver gives the solution in the rightmost column of the table, which is, as you can see, an excellent solution. Though the RMSE is about 3 times what it is in the tailored solutions, it is still at the fraction of a percent level.

This last solution illustrates that though the Solver does not necessarily find the globally best solution, the solution it does find can sometimes be improved upon. Another approach to doing this is to observe that as both calcium and sulfate are low in the

solution that we got starting from 0 for all additions, adding additional calcium sulfate might help. A little experimentation shows that increasing calcium sulfate to 1320 mg/L decreases the magnitude of the calcium error to  $-1.29$  mg/L ( $-0.4\%$ ) and sulfate error to  $-4.16$  mg/L ( $-0.5\%$ ). This action alone yields an RMSE of  $0.385\%$ , which is a big improvement over  $2.4\%$ , but running the Solver after this manual adjustment gets us an RMSE of  $0.018\%$ , which is as good a solution as we got in the first instance with all the manual tweaking.

Thus it is possible to get good solutions from the Solver when it starts from 0 mg/L for all salts and acids. Nevertheless we encourage brewers to at least try to get started with manual additions because the process of using them will teach you what to expect from a given addition of a given salt or acid and, in the process, enhance your understanding of brewing water chemistry.

## SAMPLE PROBLEMS

In this section we list some problems that can be solved using the spreadsheet and their solutions. Many of these are here in order to illustrate the flexibility of the spreadsheet, i.e. that it is capable of doing many things that may not at first be obvious.

**Problem 1:** What is the equilibrium pH of distilled water in contact with the atmosphere, at  $20^\circ\text{C}$  and how much carbon dioxide is dissolved? What is the alkalinity of this water? Assume that the partial pressure of carbon dioxide in air is 0.0003 atmospheres. What happens if distilled water is placed in a keg pressurized to 14.7 psig (2 atm psia) at  $20^\circ\text{C}$ ? At  $2^\circ\text{C}$ ?

**Solution 1:** Distilled water initially has nothing dissolved in it. Placed in contact with the atmosphere, carbon dioxide will dissolve, forming carbonic acid, some of which will convert to bicarbonate, giving up protons, which lower the pH, in the process. When the (negative) charge on the bicarbonate ions equals the (positive) charge of the hydrogen ions, the system is at equilibrium. To solve the problem we first specify distilled water in the Source part of the spreadsheet by setting 'C' in A21 and 0 in C21. All other ion input cells should also be 0. Source water pH should be set to 7, the pH of distilled water. Set the temperature to  $20^\circ\text{C}$ . The end point pH can be whatever you like – 4.3 is fine. Now we add bits of carbo by increasing C21 while watching the Imbalance in E55 and the partial pressure of carbon dioxide in C 70. Setting C21 to .01, for example, causes an electrical imbalance of  $-98\%$  and a partial pressure of 0.00005 atm. As we know the pH of water with dissolved  $\text{CO}_2$  is lower than neutral, we can start decreasing the pH in C3. Setting it to 6, for example, reduces the imbalance to  $-49\%$  and at the same time increases the partial pressure to 0.00018. We are going in the right direction

Clearly, this is a job for the solver. To set it up have the Solver vary C3 and C21 to zero the imbalance (F55) subject to the constraint that the partial pressure (C70) be 0.0003.

Before turning the problem over to the Solver, you should have a look at where things stand. With a pH of 6 we find the imbalance improved relative to 7 but still not good. F53 shows cations at 0.001 mMol/L while anions are at triple that level at 0.003. To improve this ratio decrease pH incrementally. At pH 5.9 anions are double cations; at pH 5.8 they are about the same. If the solver is deployed with this value for pH, it should be able to find a solution. If it has trouble and you know that your trials are taking you in the right direction, keep going manually. The closer you are to the solution when the problem is turned over to Solver the better its chances. The solution is pH 5.65, carbo 0.014 mMol/L. As this all started as carbon dioxide, that means that  $0.014 \times 44 = 0.62$  mg is dissolved in each liter, producing 0.49 mg/L carbonic acid and 0.13 mg/L bicarbonate.

For the second part of the problem we proceed in the same way except that we set the constraint that C70 have a value of 2. Alternatively we can set up the problem so that the solver sets C70 to a value of 2 subject to the constraint F55 be 0. In either case the solver will find pH 3.741 with total dissolved carbo of 78.77 mol/L. A look at cell C32 shows that 4874.6 mg (i.e 4.8 grams) of  $CO_2$  are dissolved in each liter of the water and C72 shows that this is equivalent to 1.75 volumes (i.e. the gas in 1 liter of the water if extracted and cooled to  $0^\circ C$  at 1 atm would have a volume of 1.75 L). Because the pH of the water at 3.74 is less than the end point pH of 4.3 alkalinity is meaningless.

Now enter  $2^\circ C$  in cell C4 and run the Solver again. The pH drops slightly to 3.694 but the amount of dissolved  $CO_2$  is (C32) nearly 9 grams/L and the volumes have nearly doubled to 3.2L/L.

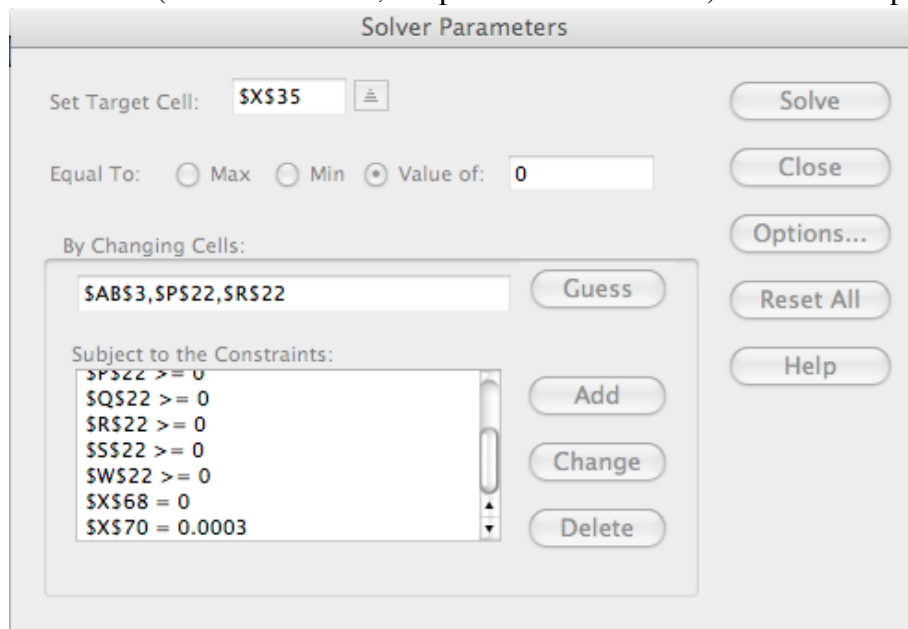
**Problem 2:** What is the pH of distilled water in equilibrium with the atmosphere *and* calcium carbonate (chalk or limestone are placed in a beaker and the beaker is filled with water), and what is the alkalinity and hardness of the water that results? What is the effect of a higher partial pressure of  $CO_2$ ?

**Solution 2:** This is a similar problem to Problem 1 and is significant because most ground and surface water are essentially like this, i.e. in simultaneous equilibrium with limestone over or through which they run and, in the case of surface water, atmospheric carbon dioxide, or, in the case of ground water, subterranean carbon dioxide produced by respiring soil bacteria. Put another way, the water you encounter from a well or water authority has been synthesized by adding limestone and  $CO_2$  to rain water. We will solve the problem by approaching it in this way.

Start by specifying deionized source water. Set pH in Cell C3 to 7.00; set the carbo input mode to 'C' in Cell A 21 and the carbo amount to 0 in Cell C21. Set all other ion concentrations in the Source area to 0. Now set all mineral, acid and salt inputs in Row 22 to 0 (Synthesis area). Now enter 10 mg/L  $CaCO_3$  in Cell P22 and 10 mg/L  $CO_2$  in R22. Set the target pH (Cell AD3) to 7. The proton deficit indicator turns red, showing that this water is imbalanced, so add more  $CaCO_3$  until approximate balance is reached. This will require about 16.2 mg/L. Note that the "Pa  $CO_2$ " annunciator is red and that cell X70 indicates that the solution we have just "made" would be in equilibrium with

0.0025 atmospheres  $CO_2$ , which is 8 times higher than the average 0.0003 atm. Note also from Cell X69 that the solution is undersaturated with respect to (can dissolve more)  $CaCO_3$  by 2 p-units. To gain insight try increasing the pH to 8. The proton annunciator says more  $CaCO_3$  is required for balance. Increasing to 22.3 mg/L will restore proton balance and result in water that is still undersaturated by about 0.8 p-units with respect to  $CaCO_3$  but which would be in equilibrium with the 0.0003 atm of atmospheric  $CO_2$ . Clearly we have come in the right direction. To find the amounts of  $CO_2$  and  $CaCO_3$  and the resultant pH, we ask the Solver to vary pH,  $CO_2$  and  $CaCO_3$  subject to the constraints that the saturation pH equals the actual pH (Cell X68 = 0) and that the equilibrium partial pressure of  $CO_2$  be 0.0003 atm. The Solver window will look as it does in the screenshot above. Note that the author leaves constraints such as “\$W\$22 >= 0” set up at all times because there is no problem that will ever want to allow these inputs to be less than 0.

The Solver will find (non-ideal model, temperatures set to 20°C) a solution at pH 8.3231, and indeed of surface and water has this is the pH most water ground that



equilibrated with the atmosphere. A look at the parameters in Col X shows that this water will have an alkalinity (end point 4.3) of about 45 ppm and a calcium hardness of about 43 ppm, both as  $CaCO_3$ . Also note that 43.2 mg/L of chalk will have dissolved and that 18.7 mg/L of  $CO_2$  from the air will have been consumed to dissolve it.

An interesting question to ask at this point is what the situation would be if the partial pressure of  $CO_2$  were, for example, 10 times higher than atmospheric, which is not at all unreasonable for well water. This is easily found by changing the constraint on X70 to 0.003 and solving again. Solver will find a solution at pH 7.66, and the alkalinity and hardness will be seen to have approximately doubled. But the amount of dissolved  $CaCO_3$  is now 94.2 mg/L and 44.8 mg/L of  $CO_2$  is dissolved from the air to do it.

**Problem 3:** A brewer grows *Brettanomyces* culture in a broth to which he adds an excess of  $\text{CaCO}_3$  to keep the pH from falling as the yeast produce acid (which Brett do) during fermentation. If the yeast produce 10 mg/L acetic acid, what will the pH of the broth be? What will it be for 20 mg/L? This question was posted to HBD in May 1990.

**Solution 3:** The interesting thing about this problem is that the answer doesn't depend much on the amount of acid the yeast produce. Carbon dioxide will be seen to have the dominating role (at least at the levels of acid production we are considering here).

The solution to the problem depends on knowing what the partial pressure of  $\text{CO}_2$  over the broth will be. Let us start by assuming that the culture is in a vessel such as an open beaker over which atmospheric air is circulated by a fan. We recognize that this is not probably the best way to maintain a yeast culture – even one of *Brettanomyces*. The state in which the NUBWS is found at the conclusion of the solution to Problem 2 (for 0.0003 atm  $\text{CO}_2$ ) is a good one for initializing the Solver to solve this problem, so repeat the steps from Solution 2 as necessary to get to that state. Note that the pH is 8.3231 (four decimal places is pretty ridiculous for pH but we are looking for small, theoretical changes here).

Now edit Cells (O:X,86) for acetic acid. Enter 4.76 in P86 for the first pK (acetic acid is monoprotic) and 40 in (Q:R,86) for the other 2 pKs. The molecular weight is 60.05 and the density of 100% acid is 1.048 g/cc. The name root is “Acet”. As we are not concerned with the salts, nothing needs to be entered in the water of hydration columns (nor the density column either). We are using acetic acid here, as *Brettanomyces* produce a lot of this acid. Enter 6 in V19 to select acetic acid. “Acetic” will appear in V21 (and in several other places as well).

Add 10 mg/L acetic acid in V22 (the proton deficit annunciator will light) and then run the Solver as for Problem 2 (0.0003 atm). Check that the equilibrium  $\text{CO}_2$  pressure in X70 is 0.0003 and that the SI (difference between saturation pH and actual pH) in X68 is 0. Note that the new pH is 8.2975 – a change of 0.0256 pH. Set the acetic acid input to 20 mg/L and run the Solver again. The pH changes to 8.2739, which represents a shift of about the same amount. Note, however, that with 20 mg/L acetic acid the dissolved  $\text{CaCO}_3$  is 55.3 mg/L as opposed to 43.2 for no acetic acid (Problem 2), so the acetic acid is dissolving  $\text{CaCO}_3$  but the carbo system is buffering pH.

Now let's assume that the brewer acts in the more usual fashion and places broth, yeast and chalk in a closed flask, i.e. one equipped with an airlock or covered by Parafilm or plugged with cotton wool. The  $\text{CO}_2$  produced by the fermenting yeast will not be able to escape and the partial pressure of the gas in the flask will approach 1 atm. Running the problem with 0 HAc (Acetic acid) and 1 atm reveals that 462 mg/L of  $\text{CaCO}_3$  will be dissolved, that it takes 1389 mg/L of  $\text{CO}_2$  (which comes from the fermentation in this case) to do it, and that the pH will be 5.8460 at equilibrium.

It is necessary to state emphatically that we are only calculating thermodynamic equilibrium states here. Should the yeast be unable to produce 1.4 grams of  $CO_2$  for each liter of broth (plus enough to fill the flask's headspace), or should there be less than 462 mg chalk for each liter of broth, or should air currents penetrate the flask such that the partial pressure of  $CO_2$  is less than 1 atmosphere, then the equilibrium we have calculated will never be reached.

Assuming that it will, we can now add 20 mg/L HAc to V22 and run the Solver one more time to see what happens. Doing so, we find the pH has declined to 5.8405 but that dissolved chalk is increased to 472 mg/L and the  $CO_2$  required to dissolve it has decreased to 1379 mg/L. Thus, again, the acetic acid produced by the yeast has little effect on the system pH, whereas the  $CO_2$  produced by them has a profound effect.

**Problem 4a:** Problems 4a – 4x are related and illustrate various aspects of NUBWS use. A brewer has heard about a commercial product for homebrewers whose manufacturer says it will set mash pH to 5.2. As he is currently studying chemistry in college and the class is learning about buffers he wonders what insight NUBWS might be able to lend. His water, which we are going to synthesize as the solution to this first part of Problem 4, has an alkalinity of 100 ppm as  $CaCO_3$  which is, in terms of Problem 4 as in many if not most brewing water problems, its most important aspect. We will also give it 20 mg of sulfate just to make things a little more interesting, specify a pH of 7 for it and assume the only cation is calcium. Thus problem 4a is: How much carbo and how much calcium does it take to produce a water at pH 7 with an alkalinity of exactly 100 given that it contains 20 mg/L sulfate?

**Solution 4a:** The reader may immediately think of specifying distilled water in the Source area and then adding calcium bicarbonate,  $CO_2$  and sulfuric acid in the Synthesis area until a proton balanced solution with the desired alkalinity is found and that approach would certainly work. Another approach, the one we will use here, is to set pH to 7, temperature of 20° C, end point pH of 4.3 and non-ideal model into the Source<sup>13</sup> area with all other values set to 0 except Sulfate (C37) which should be set to 20 g/L and then ask the solver to set the electrical balance (F54) to 0 by varying carbo (C21; A21 set to 'C') and calcium (C22) subject to the constraint that the alkalinity (C57) is to be equal to 100. Solver calculates 2.41 mmol/L carbo required with 47.8 mg/L calcium (119.2 ppm as  $CaCO_3$ ). The resulting water has the desired 100 ppm as  $CaCO_3$  alkalinity, a residual alkalinity of 65.9 ppm as  $CaCO_3$ , would give an upward pH shift of 0.11 relative to a distilled water mash and has 100 ppm as  $CaCO_3$  temporary hardness (no surprise here) with 19.2 ppm as  $CaCO_3$  permanent hardness.

---

<sup>13</sup> If the reader is following along and working the problems he may wish to use the Dilution area rather than the Source area as he will be setting the Source area for distilled water in subsequent parts of Problem 4. This is an example of using the Dilution area as a place for a “scratch” water.

**Problem 4b.** Our brewer has obtained the MSDS (Material Safety Data Sheet) for the product which reveals that it is a phosphate buffer. What is the composition of a phosphate buffer for pH 5.2 at a level of about 1 tbsp (approximately 15 grams) per 5 gallons? What is its molar strength and buffering capacity?

**Solution 4b:** Our brewer has been taught that buffers work best at a pH within one pH unit of one of the pKs of the acid on which the system is based (phosphoric in this case) and worst half way between. He observes, from (O:S, 85), that 5.2 is pretty close to half way (4.66) between the first 2 pK's of phosphoric acid and is 2.01 pH units from the nearest pK at 7.21 but being curious as to what the consequences of this might be he presses on. He starts by setting up the Source Area for distilled water: pH 7, all ions 0, carbo mode to 'C' and carbo (C21) to 0. He sets all entries in the Synthesis Area to 0 and the Target Area pH to 5.2. He notices right away that the proton deficit fields (X,35:36) have turned red telling him that he needs to add acid to lower the pH of even distilled water to 5.2 (though not very much). He enters 3 in X24 indicating to the spreadsheet that he will be using phosphates, checks that V21 is set to 1 enters 'Na' at V24 and 'K' at W24 because he plans to balance the cations between sodium and potassium rather than have all of one and none of the other. (V,25:26) now reads "mg Monobasic Sodium Phosphate" (this is the acid) and (W,25:26) "mg Dibasic Potassium Phosphate"<sup>14</sup>. He sets J75 to 5 gallons because he knows the recommended dose of the product is 1 tbsp (about 15 grams) per 5 gal.

He now enters 100 mg/L monobasic sodium phosphate at V27 and checks V78 which shows that this is equivalent to 1.9 grams in 5 gallons. This is a reasonable place to start. Note that the proton imbalance in Z35 is only -0.0012. This seems like a very small amount so he adds some dibasic potassium phosphate until the solution is balanced (Z35 is 0) and finds that only 0.21 mg/L are required. Looking at (W78) he sees that only 4 mg of this salt are required to treat the whole 5 gallons which is insignificant relative to the weight of the monobasic salt. Based on the recommended dose for the commercial product he increases the monobasic salt to 800 mg/L noting that this results in 15.14 grams total and then readjusts the dibasic salt to re-zero Z35 and finds that 10.27 mg/L is sufficient which amounts to .194 gram for the 5 gallons and a total of 15.33 grams of salts added which is close enough to 15 grams to be relevant.

(V:W,50) shows that the buffer consists of 6.59 mMol/L monobasic salt and 0.058 mMol/L dibasic salt for a total molar strength (W61) of 6.72 mMol/L. A quick glance at Z41 shows him that his sodium would be at 153 mg/L and this prospect doesn't please him. To check the buffering capacity of the buffer he changes the pH in AD8 by a small amount, 0.05 pH to 5.25 and notes that the proton deficit is -0.0099. This means that if the buffer is stressed by adding base which consumes 0.0099 mEq/L of protons the pH would rise by 0.05 units so the buffering strength is  $0.0099/0.05 = 0.198 \text{ mEq-L}^{-1}/\text{pH}$ . This

---

<sup>14</sup> Note that the choices here are arbitrary. A phosphate buffer can be made with both sodium salts, both potassium salts or one of each.

is not very impressive performance especially when compared to Kolbach's estimate of the buffering capacity of malt at 11.905 mEq-L<sup>-1</sup>/pH.

**Problem 4c:** Our brewer remembers that distilled water mashes of pale malts generally go to a pH of about 5.75 and that malt contains a lot of phosphate. What would be the composition of a phosphate buffer at pH 5.75 with buffering capacity 11.905 mEq-L<sup>-1</sup>/pH?

**Solution 4c:** The spreadsheet should still be set up for distilled water as the source. The brewer obtained a buffering capacity of 0.198 mEq-L<sup>-1</sup>/pH with 800 mg/L monobasic sodium phosphate and needs 11.905. He designs buffers with 1600, 3200, 6400, and 12800 mg/L monobasic sodium phosphate and calculated the buffering capacity for each. He plots these capacities against the monobasic salt concentration and does a linear fit finding that the buffering capacity is approximately  $Q = 0.9m - 0.4$  where  $m$  is the number of grams of monobasic salt per liter. Solving for  $m$  when  $Q$  is 11.9 gives 13.667 grams as the approximate amount he'll need. He designs a buffer with 13,667 mg/L monobasic salt and checks its buffering capacity which comes out to 12.016 so he tries one at 13,500 mg/L and finds it has a capacity of 11.86. He interpolates between these two buffers and comes up with 13,549.2 as the amount of monobasic salt required for 11.905 mEq-L<sup>-1</sup>/pH buffering capacity. It needs 881.72 mg/L dibasic salt and the total buffer strength is 117.98 mMol/L.

(Z,54:57) show this buffer puts 2 mg/L phosphoric acid, 10949 mg/L monobasic phosphate ion, 488.1 mg/L dibasic phosphate ion and 0.0001 mg/L tribasic phosphate ion for a total of 11,439 mg/L phosphate into the water. In 5 gallons which is 18.927 liters there would then be 216.51 grams of phosphate in its various forms. Each gram of phosphoric acid derives from 0.724 grams of phosphorous pentoxide which reacts with water to form the acid:  $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$ . Thus 216.51 grams of phosphate would be reported as 156.75 grams "as the pentoxide" and our reason for doing it this way is that malt phosphate content is often reported in these terms. Assuming mash thickness is 1 quart per pound of malt there would be 20 pounds or about 9080 grams of malt in this volume of water. 156.75 grams is about 1.7% of this. Malt is reported in Ref. 9 to contain about 1% phosphate as the pentoxide and while the number calculated by our man is appreciably larger than this it is satisfying to him that things check out in this regard if only approximately.

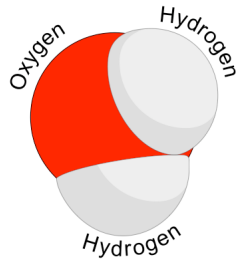
Our brewer notes that the amount of sodium reported in Z46 is huge and realizes that the phosphate in malt isn't paired with that much sodium but rather a mixture of sodium, potassium, magnesium and calcium ions. The cation(s) involved have little effect on the performance of the buffer (and that through ionic strength).

---

<sup>15</sup> Note that the choices here are arbitrary. A phosphate buffer can be made with both sodium salts, both potassium salts or one of each.

## Appendix A: Basic Water Chemistry

Water is a simple chemical compound made up of two hydrogen atoms and one oxygen atom. Hydrogen atoms have one proton (a positively charged particle) and one electron (a negatively charged particle). The charges are equal but have opposite sign. On the other hand, the mass of the proton is some 1823 times the mass of an electron. In oxygen there are 8 protons, 8 neutrons (uncharged particles with mass about the same as that of the proton) and 8 electrons. Two of these are found close to the nucleus (the part of the atom that contains protons and neutrons) and 6 in a shell of slightly larger radius. The atom is much more stable if the second shell has 8 electrons in it, and so it attracts the electrons in each of two hydrogen atoms by pulling their electrons into its outer “shell”. Thus a water molecule (a combination of atoms) looks sort of like Mickey Mouse with spherical ears (separated by  $104.45^\circ$ ). The hydrogen atoms, i.e. they are have a partial share in their most of their time closer to the oxygen end of the molecule has the hydrogen’s oxygen end of the molecule has the “ears” has a positive charge. water many of its properties.

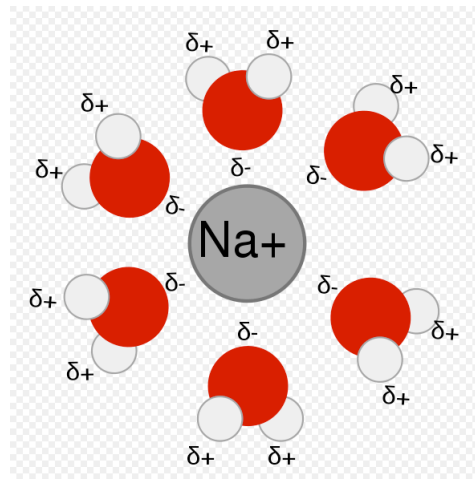


“ears” are the remains of the made up of the protons that still electrons, though those spend oxygen atom. Because the oxygen electrons most of the time, the a negative charge while each of This separation of charges gives

For example, it may seem likely that there would be mutual electrical attraction between one of the positively charged regions (white in the picture) of one molecule and the negatively charged

This is indeed the case, always arranging and into groups of several small one shown in the bonding between as hydrogen bonding, than the one in the would be that water many of its

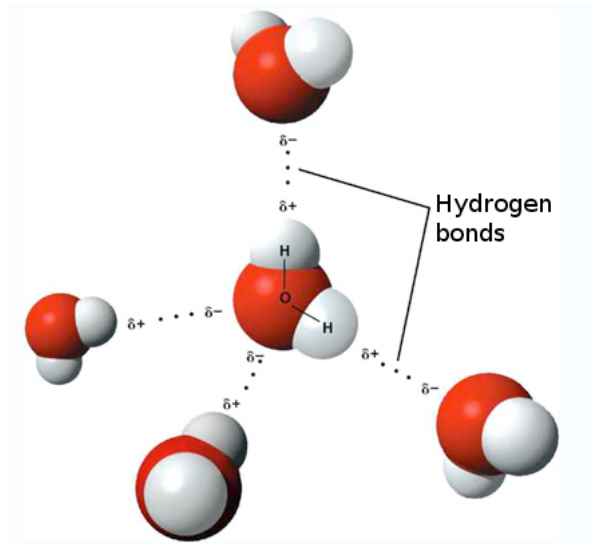
From this second evident that a better water would be modest integer.



region (red) of another. and water molecules are rearranging themselves molecules such as the picture below. This molecules is referred to and a better statement previous paragraph hydrogen bonding gives unique properties.

picture it should be chemical formula for  $H_{2n}O_n$  where  $n$  is some

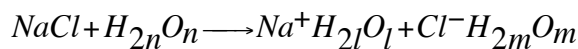
When certain types as table salt (sodium chloride) are placed separate not into atoms but rather into this example the charged chloride ion, positively charged This is because chlorine have 7 outer shell and, like They tend to take like sodium that have outer shell and so to leave themselves outermost shell (the in which the taken electron was originally found) and a net positive charge.



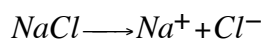
of substances such chloride), for in water they their constituent charged ions, in negatively  $Cl^-$ , and sodium ion,  $Na^+$ . atoms like electrons in an oxygen, want 8. one from atoms 1 electron in an readily give it up with a complete one below the one

Positively charged ions attract the negatively charged round end of water molecules, and negatively charged ions the positively charged bumps. Thus ions are surrounded by “solvation sheaths” of water molecules with the protons (remains of hydrogen atoms) facing away from the ion in the case of positively charged ions. Conversely, a similar picture applies to the chloride ion, which, as it is negatively charged, would have the  $\delta+$  charges facing it. In the sodium picture here there is, of course, no reason why the  $\delta+$  outside the ring of water molecules could not form hydrogen bonds with the  $\delta-$  charges of other water molecules not shown in the picture, and they do. Solvated ions can be readily transported among other water molecules because of these sheaths.

A chemical equation for the solvation of sodium chloride could therefore be written as



where  $n=l+m$  are all integers. In order to simplify notation we usually don't write the water molecules at all, but simply



The reader is to understand that the actual mechanism of separation involves the solvation process as described here.

The amount and type of ions in a water sample determine its characteristics and suitability for brewing. For many things which dissolve in water the chemistry is as simple as described above (simplified form) for sodium chloride. If a quantity of sodium chloride containing  $n$  molecules is placed in a liter of water it will dissolve and there will be  $n$   $Cl^-$  and  $n$   $Na^+$  ions in that liter when dissolution is complete. As  $n$  will, in general, be a very large number indeed, we prefer to work with weights. To do this we

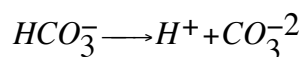
define the mole (often abbreviated to mol) as being  $6.023 \times 10^{23}$  things (atoms, ions, etc.) and then tabulate the weights of 1 mole of the things we are interested in. This weight, expressed in grams, is called the gram molecular weight of a substance. The gram molecular weight of sodium is 22.9897 grams, of chlorine 35.4528 and of sodium chloride 58.4425. Thus if we dissolve 5.84 grams of sodium chloride equal to 0.1 mol we would have 0.1 mol of chloride (which weighs 3.54 grams) and 0.1 mol of sodium ion weighing 2.298 grams.

Calcium has 2 electrons in its outer shell and so gives doubly charged ions, when its ionic compounds (salts), which contain anions (negatively charged ions) with charge totaling  $-2$ , dissolve. Calcium chloride,  $\text{CaCl}_2$ , with two chlorides each carrying a single negative charge, and calcium carbonate,  $\text{CaCO}_3$ , in which calcium is paired with the double charged carbonate ion,  $\text{CO}_3^{-2}$ , are examples. Where ions are multiply charged, chemists often speak in terms of *equivalents*, where an equivalent is 1 mole of charge. Thus 1 mole of calcium (which weighs 40 grams) carries 2 moles of charge or 2 equivalents. The *equivalent weight* of a substance is that weight which carries 1 mole of charge, so the equivalent weight of calcium is half its molecular weight or 20 grams. Equivalents are handy because one equivalent of a positively charged ion reacts with one equivalent of a negatively charged ion. Thus 1 equivalent of calcium (half a mole, 20 grams) ion reacts with 1 equivalent of chloride (1 mole, 35.45 grams) to give half a mole of  $\text{CaCl}_2$  (the number of molecules of the salt is equal to the number of molecules of calcium or half the number of chloride ions). The molecular weight of  $\text{CaCl}_2$  is  $40 + 2 \times 35.45 = 110.9$  grams, so 0.5 mole of it weighs 55.45 grams.

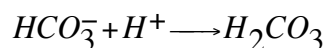
If we deal only with salts like sodium chloride and calcium chloride, it is very easy to see the effect of adding a given amount of the salt on the ion concentrations of the water. If we add 0.1 mol of sodium chloride, we add 0.1 mol sodium ions and 0.1 mol chloride ions to whatever amounts are already present. What is not so easy is to set the amounts to exactly what we want them to be. Suppose we wanted to increase the chloride ion content of brewing water by 0.1 mol (that's more than we ever would practically speaking but for illustration it will do) but don't want the sodium to increase that much. We are pretty much stuck here because the salts come with both chloride and an anion (metal ion). We clearly couldn't use sodium chloride here but may be able to use another salt, such as calcium chloride,  $\text{CaCl}_2$ , which provides 2 moles of chloride for every mole of the salt, but also adds 1 mole of calcium (which is generally less objectionable at high levels than sodium). Even with the use of other salts we probably will not be able to hit target levels of ion concentrations unless those target levels come from analysis of natural water and we use the same salts nature used when that water flowed through the ground. Even if we can't hit the target exactly, it is possible to find solutions (salt addition amounts) that give the best approximations to a desired water ion profile using well defined, relatively simple math.

The problem gets sticky when we consider salts like sodium bicarbonate,  $\text{NaHCO}_3$ , or calcium carbonate,  $\text{CaCO}_3$ , which is the chemical formula for chalk and limestone. If we

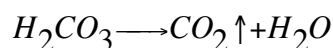
put 0.1 mol of  $NaHCO_3$  into a liter of water it will separate into 0.1 mol  $Na^+$  and 0.1 mol bicarbonate,  $HCO_3^-$ , ion (ions can be made up of several atoms), but not all of this will remain as bicarbonate. Some will give up a hydrogen ion



to become bicarbonate, and some will take on a hydrogen ion



to become carbonic acid, some of which may, in turn, decompose into water and carbon dioxide

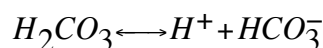


Which of these reactions will take place and the extent to which they do so depends on the acidity of the solution. If you add sodium bicarbonate to a glass of tap water and dissolve it, not that much happens, but if you add it to a glass of water to which you have added a teaspoonful of vinegar, it will fizz. Acidity is conveniently expressed through the pH (*pondus hydrogenii* or weight of hydrogen), with a pH of 7 corresponding to a neutral (neither acid nor basic) solution, values less than 7 representing acid conditions, and values greater than 7 alkaline ones. Most of the complexity of the NUBWS is involved in dealing with this subject, which is complicated by the fact that the solutions we deal with in brewing contain sufficient concentrations of ions that they cannot be considered “ideally dilute”.

### **Acids, Ratios and Fractions, Law of Mass Action, the *p* Operator**

Understand what is in this section and you are well on your way to having conquered brewing water chemistry. Unfortunately this material will be unfamiliar to those whose educations in chemistry have been limited to high school or basic college courses. It is typically studied as part of a Physical Chemistry or other advanced course, and though it may be unfamiliar it is, conceptually at least, a relatively simple extension of the basic ideas behind ionic equilibrium.

An acid is, under the definition important to us here (the Lowry-Brønsted definition), a substance that when placed in a solvent (water) gives off hydrogen ions (protons). Carbonic acid is a weak acid that gives off protons in two stages. In the first the acid releases a proton leaving a bicarbonate ion behind



The double-headed arrow shows that this reaction can also take place in the opposite direction in which a bicarbonate ion captures a proton becoming a molecule of carbonic acid.

The Law of Mass Action (Henderson-Hasselbalch Equation) gives the relative activities (close to the ion concentrations -- in ideally dilute solutions equal to the concentrations) of carbonic acid molecules, bicarbonate ions and protons through the equation

$$\frac{\{HCO_3^-\}\{H^+\}}{\{H_2CO_3\}} = K_1$$

in which the brackets represent the *chemical activity* of the species named inside them and  $K_1$  is called the *first dissociation constant* of carbonic acid. It is related to the energy with which carbonic acid binds its first proton and is dependent on temperature.

The activity of a charged ion depends on its concentration in the solution and an activity coefficient, a number less than one that reflects the fact that in a non-ideal situation a lesser proportion of ions are available for reaction because of interactions between the ions themselves. Thus

$$\{HCO_3^-\} = \gamma_{HCO_3^-} [HCO_3^-]$$

shows the activity of bicarbonate to be the molar concentration (moles per liter) of bicarbonate (indicated by straight brackets) multiplied by an activity coefficient (a number less than but close to one, implying that in ideally dilute solutions activities and concentrations are equal) associated with bicarbonate ions (carbonate ions have a different activity coefficient).

At this point we introduce the  $p$  Operator. This operator when applied to a quantity computes its negative logarithm to the base 10 (Briggs logarithm), thus

$$px = -\log_{10}(x)$$

The rules for application of logs thus apply equally well to the  $p$  operator. In particular

$$p \frac{abc\dots}{def\dots} = pa + pb + pc\dots - pd - pe - pf\dots \text{ and } pa^n = npa$$

Applying  $p$  to the Henderson-Hasselbalch equation according to these rules gives

$$p\gamma_{HCO_3^-} + p[HCO_3^-] - p\gamma_{H_2CO_3} - p[H_2CO_3] = pK_1 - pH$$

Here we have used  $pH = p\{H^+\}$  to represent the  $p$  operator as applied to the hydrogen ion activity, as this is the definition of pH.

The determination of actual individual activity coefficients is impossible. Chemists, therefore, use approximations, some based on theory and some on measurement. In the water industry, minus the Briggs logarithm of the average activity coefficient for an ion with charge  $z_i$  is taken to be

$$p\gamma_i = z_i^2 p f_m$$

where

$$p f_m = A \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right]$$

in which  $A$  depends on the dielectric constant of the water and its temperature and

$$I = \frac{1}{2} \sum_i z_i^2 [m_i]$$

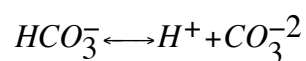
is the *ionic strength* of the solution. In the ionic strength formula  $[m_i]$  represents the concentration of (charged) ion  $i$  in moles per liter. From this it is clear that the carbonic acid activity correction would be 0, that for bicarbonate ion it is simply  $p f_m$ , but for a calcium ion,  $Ca^{+2}$  with its double charge it would be  $4 p f_m$ . Using these facts and doing some rearranging we get

$$p[H_2CO_3] - p[HCO_3^-] = pH - pK_1 + p f_m$$

Because of the definition of the  $p$  Operator and the rules pertaining to logarithms, the difference of the terms on the left hand side represents the logarithm of the ratio of bicarbonate to carbonate concentration (remember the minus sign in the definition of  $p$ ). Defining this as  $r_1$  and taking the antilogarithm (raising 10 to the power of) the right hand side gives

$$r_1 = 10^{pH - pK_1 + p f_m}$$

Following exactly the same reasoning with respect to the second stage of dissociation of carbonic acid we have



This is governed by equilibrium constant  $K_2$ , so we obtain

$$r_2 = 10^{pH - pK_2 + 3pfm}$$

for the ratio of carbonate to bicarbonate. Note that the ionic strength correction is 3 times what it was for  $r_1$ . This is because of the carbonate ion's  $4pfm$  correction minus the  $pfm$  correction for the bicarbonate.

Now let us suppose that there are  $x$  moles/liter carbonic in a given solution. There would then be  $r_1x$  moles/L bicarbonate and  $r_1r_2x$  moles of carbonate for a total of

$$C_T = x(1 + r_1 + r_1r_2)$$

From this it is clear that the fraction of  $C_T$  that is carbonic is

$$f_1 = \frac{x}{C_T} = \frac{1}{(1 + r_1 + r_1r_2)}$$

The fraction that is bicarbonate is

$$f_2 = f_1r_1 = \frac{r_1}{(1 + r_1 + r_1r_2)}$$

And the fraction that is carbonate is

$$f_3 = f_2r_2 = \frac{r_1r_2}{(1 + r_1 + r_1r_2)}$$

It will have occurred to the astute reader that you can't calculate  $pfm$  unless you know ionic strength, and that you can't calculate ionic strength unless you know  $pfm$ . This is indeed the case and we work around it by iterative calculation. This is what goes on in (B:D,80:120), (I:K,80,151), (X:Z,80:120) and (AN:AP,80:120).

**Carbonate Saturation:** Calcium carbonate is not very soluble in water. The governing equation is

$$\{Ca^{+2}\}\{CO_3^{-2}\} \leq K_S$$

where  $K_S$  is the solubility product, which depends on whether the solid form is calcite (the most common but the least soluble), vaterite or aragonite. If the product of the two ion activities is less than the solubility product,  $K_S$ , the water is undersaturated with respect to calcium carbonate and more can dissolve. If greater the water is super saturated and calcium carbonate will precipitate. If equal, the maximum amount of calcium carbonate is dissolved and no more can. The water is said to be saturated or "at

equilibrium” with respect to calcium carbonate. Applying the  $p$  operator and substituting concentrations we have, at equilibrium:

$$4pf_m + p[Ca^{+2}] + 4pf_m + p[CO_3^{-2}] = pK_s$$

Substituting for the carbonate from the Henderson-Hasselbalch equation

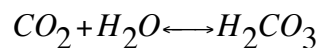
$$p[CO_3^{-2}] = p[HCO_3^-] + pK_2 - pH - 3pf_m$$

we get, at equilibrium

$$p[Ca^{+2}] + p[HCO_3^-] + 5pf_m + pK_2 - pH - pK_s = 0$$

The amount by which the left hand side differs from 0 is a measure, in  $p$  units, of how over- or undersaturated the system is with respect to  $CaCO_3$ . Setting the equation to 0, it can be solved for the pH at which water with given levels of calcium hardness and alkalinity will be saturated, or for the concentration of calcium at which the water will be saturated at a particular pH. If the solution to this equation gives a pH higher than the sample pH, the water is supersaturated with respect to calcium carbonate and will precipitate it, though this may be a very gradual process. As precipitation occurs the pH falls back and, of course, the calcium concentration goes down. These processes continue until the saturation pH (the pH obtained from the equation) equals the actual pH. At this point the water is at equilibrium. If the saturation pH is less than the sample pH, the sample is undersaturated with respect to calcium carbonate and more can be dissolved. The saturation pH and value of the left hand side are displayed in the spreadsheet.

**Carbon Dioxide Saturation:** Carbon dioxide in the air dissolves via



governed, as elsewhere, by the Law of Mass Action

$$\frac{\{H_2CO_3\}}{\{CO_2\}\{H_2O\}} = K'_{Hy}$$

usually written as

$$\frac{\{H_2CO_3\}}{\{CO_2\}} = \{H_2O\}K'_{Hy} = K_{Hy}$$

in which the activity of water, nearly a constant because the solutions are very dilute, is rolled into the equilibrium constant that is called the Henry Coefficient<sup>16</sup>. Before applying the  $p$  operator here we note that for gasses at low pressure the activity is simply the partial pressure of the gas. Thus

$$p[H_2CO_3] - pP_{CO_2} = pK_{Hy}$$

When the NUBWS analyzes water it computes the concentrations of carbonic as well as carbonate and bicarbonate. Solving the above formula for

$$P_{CO_2} = 10^{pK_{Hy} - p[H_2CO_3]}$$

gives the partial pressure of carbon dioxide that is in equilibrium with the solution. If this pressure is greater than the partial pressure of  $CO_2$  in the atmosphere (about 0.0003 atmospheres), then the solution is supersaturated with respect to  $CO_2$ , which will, though it may be a gradual process, escape the solution, causing its pH to rise. This process continues until  $P_{CO_2}$  reaches the atmospheric level, at which time the solution is in equilibrium. If, on the other hand, the partial pressure of  $CO_2$  over the solution is lower than 0.0003 atm the solution is under saturated with respect to  $CO_2$  and  $CO_2$  from the air will dissolve in it until it is at equilibrium.

If we place water in a keg and pressurize it to 14.7 psig (i.e. 1 atm above ambient or 2 atm psia) we can then play with the pH and  $C_T$  parameters until electrical balance is obtained and the calculated pressure is 2 atm. This allows us to determine how much  $CO_2$  is dissolved at a given applied  $CO_2$  pressure and what the pH of the resulting carbonated water would be. See Problem 1.

## Appendix B: Alkalinity

Alkalinity is a measure of a water sample's ability to resist pH change when acid is added to it. As such it is indicative of the water's ability to hold mash pH high which is undesirable. In potable (and brewing) water alkalinity is assumed to be caused solely by bicarbonate and carbonate ions. As carbonate constitutes less than 1% of the total carbo (carbonic + bicarbonate + carbonate) in waters at pH less than 8.3, it is bicarbonate that is responsible for most of alkalinity.

---

<sup>16</sup> Note that this is actually done with the dissociation equations as well the first of which would more formally be written as  $H_2CO_3 + H_2O \longleftrightarrow H_3O^+ + HCO_3^-$ , which recognizes that protons are actually carried on water molecules. Thus the hydrogen ion is more properly the hydronium ion and pH is really the activity of the hydronium ion. We use  $H^+$  rather than  $H_3O^+$  for compactness in notation.

Alkalinity is measured by placing a sample (usually 0.1 L) of the water to be tested into a flask into which a pH electrode or chemical indicator<sup>17</sup> is introduced. When the pH reading stabilizes, it is noted. This is the pH of the sample that goes into C3. Acid of known strength, usually 0.1 N  $HCl$  or  $H_2SO_4$  (which contain 0.1 equivalents of protons per liter or 0.1 milliequivalents/mL), is added in small, controlled amounts (titration). As this is done, the acid neutralizes the bicarbonate and the pH falls. When the pH reaches a chosen value (called the *end point*), as indicated by the pH meter reading or a color change in the indicator, the number of milliliters of acid added is noted and the number of milliequivalents (normality times volume used) is divided by the sample volume to give the number of milliequivalents per unit of sample required to reach the end point. This is the definition of alkalinity. With a 0.1 L sample and 0.1 N acid, the alkalinity is simply the number of mL of acid.

While it is perfectly acceptable (and, in the author's opinion, highly desirable) that alkalinity be reported in mEq/L (sometimes called millival or mval), it is customary in the United States to multiply by 50 to obtain units of "milligrams per liter as calcium carbonate," sometimes abbreviated as "ppm as calcium carbonate". This is because a liter of distilled water in which 100 mg of limestone has been dissolved *by the action of carbon dioxide* (which is how Mother Nature does it) will have an alkalinity of 100 ppm as calcium carbonate higher than that of the distilled water. Distilled water has finite alkalinity because it requires a finite amount of acid to lower the pH of distilled water to a value less than 7 (most distilled water already has a pH somewhat lower than 7 because carbon dioxide from the air has dissolved in it).

The value of alkalinity determined for a particular sample clearly depends on the choice of end point. Unfortunately, there is no standard end point. Standard Methods for the Examination of Water and Waste Water, incorporated by reference into the ASBC Methods of Analysis, requires only that the laboratory report the end point with the alkalinity number. Most laboratories do not do this. In brewing 4.3 is a sort of *de facto* standard.

A common practice is to choose the end point to be the pH at which the hydrogen ion concentration and bicarbonate ion concentration are equivalent (the same). Thus the more bicarbonate present the lower the end point pH. This clearly requires *a priori* knowledge of the carbo content of the water, but is usually handled in terms of a recommended end point for various expected ranges of alkalinity.

The spreadsheet can be used to determine the equivalence end point for a given level of alkalinity. Enter that level at C21 (ensure that there is an 'A') in A21 so that the number will be interpreted as alkalinity. Now examine H16 and vary D3 while continuing to do so. The value in D3 that zeroes H16 is the end point pH for this level of alkalinity (and sample pH, C3). One can of course use the Solver to find the correct value for D3.

---

<sup>17</sup> An indicator is a substance that has color determined by the pH of the solution in which it is dissolved. Phenolphthalein is probably the best known indicator. It is red at pH > 8.3 and colorless at pH < 8.3

The *total alkalinity* is determined by titration to the end point as discussed above, and it is this alkalinity, sometimes referred to as *m-alkalinity* because the indicator methyl orange was traditionally used to detect the end point, with which we are concerned as brewers. If the original sample pH is greater than 8.3 the amount of acid required to get to 8.3 is sometimes recorded separately and this amount is called the *p-alkalinity* because pH 8.3 is the pH at which phenolphthalein, the indicator traditionally used for this first titration (when sample pH > 8.3), changes color from pink to clear. In this case the second indicator will be added (phenolphthalein is clear when pH < 8.3) and titration continued until the second (m) endpoint is reached. The total acid used is the total alkalinity.

The alkalinity titration rearranges the relative distributions of carbonic, bicarbonate and carbonate. Two things happen that require acid. Bicarbonate is converted to carbonic and carbonate is converted to bicarbonate. Thus if there are  $C_T$  (see Appendix A for the meaning of this and the other symbols used here) millimoles of carbo per liter in the sample,  $C_T(f_{1,e} - f_{1,i})$  mmol/L acid will be required to bring about the observed increase in carbonic (the letter subscripts refer to the end point and initial (sample) fractions, respectively), and  $C_T(f_{3,i} - f_{3,e})$  more will be needed for reduction of the concentration of carbonate.

As noted in Appendix A, the pH is minus the Briggs log of the activity of hydrogen ion

$$pH = p\{H^+\} \approx pfm + p[H^+]$$

so that the hydrogen ion concentration is

$$[H^+] \approx 10^{pH - pfm}$$

and a shift in pH from  $pH_i$  to  $pH_e$  will thus require

$$1000 \left[ 10^{pH_e - pfm_e} - 10^{pH_i - pfm_i} \right] \text{ millimoles (that's what the factor of 1000 is for)}$$

of hydrogen ion to set the end point pH over and above that which is required to convert bicarbonate and carbonate. Finally, there must be hydroxyl ion concentration reduction of

$$1000 \left[ 10^{pK_w - pH_i - pfm_i} - 10^{pK_w - pH_e - pfm_e} \right] \text{ mEq/L}$$

and each of these requires 1 mEq/L acid to neutralize it to water. Thus the total requirement is

$$alk = C_T [(f_{1,e} - f_{1,i}) + (f_{3,i} - f_{3,e})] + 1000 \left[ 10^{pH_e - pK_w} - 10^{pH_i - pK_w} + 10^{pH_e - pK_w} - 10^{pH_i - pK_w} \right]$$

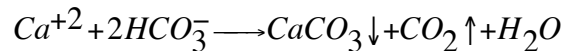
and this is the alkalinity.

In the usual case, we are given a laboratory's sample and end point pH values and the total alkalinity, and we need to determine  $C_T$  for which this equation can clearly be solved. We have also, however, given the spreadsheet the capability to work from specification of  $C_T$ , in which case it can calculate the alkalinity from the two pH values.

### Appendix C: Reducing Alkalinity (Decarbonation)

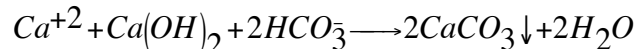
As alkalinity is a measure of the water's ability to resist reduction in pH to values that we need in the mash tun for effective enzyme performance where alkalinity is high we need to reduce it. The following summarizes several of the popular methods.

**Heat:** In potable and brewing water alkalinity is caused by the presence of the bicarbonate ion,  $HCO_3^-$ . For each one of these ions present in a given volume of water there must be an equal amount of charge born by cations in order that the solution be electrically neutral. Calcium ions can combine with bicarbonate ions to form slightly soluble calcium carbonate, water and carbon dioxide

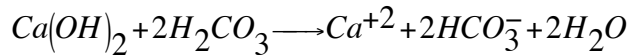


under favorable conditions. These include the presence of nucleation sites onto which the  $CaCO_3$  can precipitate, heat that makes  $CO_2$  less soluble so it leaves the solution readily (thus pushing the reaction to the right by Le Chatelier's principle), high pH that converts  $HCO_3^-$  to  $CO_3^{2-}$ , a gas to sparge out the  $CO_2$  as it forms, and high (perhaps supplemented) calcium ion content that also pushes the reaction to the right by Le Chatelier. Often brewers simply heat the water as far as boiling, in which case the steam formed is the sparging gas, but it is not necessary to reach boiling if some other gas (such as air from a compressor) is sparged through the water or if the hot water is sprayed through a nozzle or shower head. Addition of a small amount of chalk (calcium carbonate) can provide the nucleation sites, and supplementation of calcium with gypsum or calcium chloride, which if they are going to be done for other reasons, anyway, should be done before heating in order to help this reaction along.

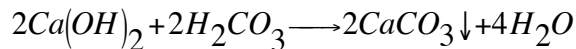
**Lime Treatment:** If lime is added to water that contains bicarbonate ion and calcium is also present (i.e. if the water has temporary hardness) these will react to form calcium carbonate and more water



For effective decarbonation obviously the majority of the total carbo should be in bicarbonate form implying a pH near 8.3. Lime is a base and tends to raise the pH of any water to which it is added neutralizing any carbonic acid (converting it to bicarbonate ion) as it does so.



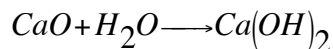
This bicarbonate (and the released calcium ions) then react with additional lime to precipitate chalk as given above. The overall reaction is:



Thus the NUBWS must calculate the amount of lime necessary to precipitate both the carbonic and the bicarbonate. To decarbonate water the calculated amount of lime is added to a small amount of water and mixed into a slurry. This is stirred into about one-half of the water to be treated allowed to react for a few minutes. The pH will go quite high and an insoluble gel of magnesium hydroxide will form if the water has appreciable magnesium content. If it does and it is desired to remove some of this magnesium, decant the water off the gel into another container. This is referred to as *split treatment*. If not, skip this decantation and just add the remainder of the water gradually, with more stirring, while the pH is monitored. If the pH reaches a value of 8 or a little less when all the water has been returned, then the amount of lime added is about correct. If the pH is appreciably higher than 8 after all the water has been added, then too much lime was used. The simplest solution to this, of course, is to add more water until pH 8 is obtained. Alternatively one can bubble  $CO_2$  through the water until a pH near 8 is reached. If pH 8 is approached before all the water is added, then not enough lime was added. One can simply add a bit more and continue in this event.

The water is allowed to sit while the chalk (calcium carbonate) precipitates and then is decanted. As with heat treatment, adding a teaspoonful of chalk before the lime supplies nucleation sites and thus helps the precipitation process along. Calcium supplementation aids the second reaction by Le Chatelier's principal. In other words, if you are going to add gypsum or calcium chloride to the water before you brew with it do that before lime treatment if you wish maximum decarbonation.

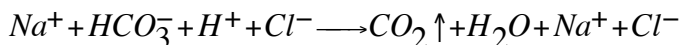
In the foregoing discussion we have assumed that slaked lime, which is readily available in the canning section of supermarkets as "pickling lime", will be used. If quicklime (it should be food grade) is used instead it will immediately react with water to produce slaked lime:



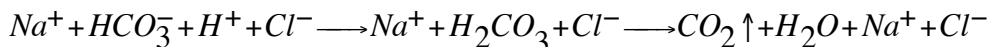
which then reacts as above, so that on a molar basis the same amount of quicklime or slaked lime is required. The spreadsheet calculates gram amounts for slaked lime. If quicklime is being used, the formula in cells C71, AB71 and AO71 can be edited to replace the gram molecular weight of slaked lime, 74.09, with that of quicklime, which is 56.077. If this is done, then the labels in Cells B71, AB71 and AN71 should also be changed to read “CaO” instead of “Ca(OH)2”. Or the slaked lime number can be multiplied by the ratio of the molecular weights, 0.757, to get the required quicklime amount.

**Addition of Acid:** A third method of reducing alkalinity is to “neutralize” it with acid. We put neutralize in quotes because the term usually is taken to mean adding an acid to a base to bring the pH to 7. In dealkalinizing water we do not necessarily strive for pH 7 but in fact for whatever pH in the liquor is necessary to get the mash pH to its desired value (5.2 – 5.7).

We will start with a simple description and then demonstrate how application of the NUBWS to this problem can lend a lot of insight into this problem. Consider a solution of sodium bicarbonate (baking soda) in water and what happens when acid (we’ll use hydrochloric) is added to it. You can try this yourself using acetic acid (vinegar). As you probably know, adding vinegar to a solution of baking soda will cause it to fizz. The result is the same for potassium bicarbonate, calcium bicarbonate, etc. With hydrochloric acid the reaction is



What this overall equation does not show is that there are two steps



In the first step the proton ( $H^+$ ) from the acid attaches to the bicarbonate ion, canceling its charge and forming a carbonic acid molecule. In the second the carbonic acid molecule decomposes into molecules of water and  $CO_2$ , some of the latter of which escapes the solution. It is the first step that removes bicarbonate (by converting it to carbonic) and thus reduces alkalinity. If acid were added to a bicarbonate solution under positive  $CO_2$  pressure such that the solution couldn’t fizz, i.e.  $CO_2$  couldn’t escape, the alkalinity would, nonetheless, be reduced. Where  $CO_2$  does escape, the pH of the water falls back closer to what it was before the acid was added. We will see how both of these things come to be when we apply the NUBWS to this situation.

Probably the most convenient place to add acid is in the mash tun. Where the malt itself supplies little or no acid (i.e. pale beers), the Residual Alkalinity (in mEq/L) is an approximate measure of the amount of acid likely to be required. Thus, for example, if water has a residual alkalinity of 1 mEq/L (50 ppm as  $CaCO_3$ ), a mash involving 100L of this water would require around 100 mEq of acid. If 1 N acid is available, the brewer

could measure out 100 mL, dough in, check pH, add say half the acid, mix and check pH again. If the pH is still high, he then adds increments of the remaining acid until he reaches the desired dough in pH or all the acid is used. If pH is still low, he then measures out more acid and continues to make additions until the desired pH is reached. With experience, of course, he will know exactly how much to add in one bolus or to the mashing water.

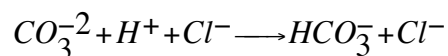
We'll note that Reinheitsgebot forbids the addition of acid for any purpose. Kohlbach's seminal paper of 1951 (Ref. 2) is most often cited for its definition of Residual Alkalinity but much of the material in it is devoted to the proposition that German brewers should be allowed to add acid for mash pH control.

The following material may be omitted on a first reading. Consider a water sample that comes to us at pH 8.3 with 3 mmol/L carbo. Set the model to ideal (0 in C2), pH to 8.3 (C3), temperature to 20 °C (C4) and enter 3 mmol/L carbo (in C21 with A21 set to "C") and 68.9132 mg/L sodium into C41 in the Source Area of the spreadsheet. This will give balanced water (set all other ions to 0) with alkalinity (to 4.3 end point) of 151.20. Cells (C,15:17) show us that 98% of the carbo is bicarbonate, with the remaining 2% about equally split between carbonic and carbonate at this pH. Notice (C70) that the partial pressure of  $CO_2$  necessary for equilibrium is 0.00085, which is larger than atmospheric  $CO_2$ , so this solution is slightly oversaturated. At this level of oversaturation, migration of  $CO_2$  into the air will be very slow.

Now set the same temperature, end point pH, carbo and sodium levels (zero all other ions) in the Target Area but change the pH to 6.3. Cells (AB,15:17) show that at this pH 55% of the carbo is carbonic and only 45% bicarbonate. Simply by conversion of bicarbonate to carbonic, the alkalinity of the water is reduced to 71.2 (AB57), i.e. by more than half.

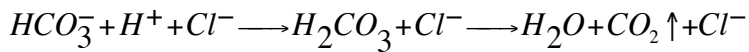
Some of the carbonic acid will convert to water and  $CO_2$ . The partial pressure of  $CO_2$  required to keep the gas in equilibrium (i.e. in solution) is 0.04 atm, almost 50 times what it is at pH 8.3, so that some of the gas will leave the solution, especially if the water is heated, as in the HLT, or agitated.

Cells (AE:53,55) in the Target Area will show an electrical imbalance because we have not considered how we got the pH to 6.3. This is done by adding acid, and for illustration we will assume that this acid is hydrochloric ( $HCl$ ). Three reactions take place. By reference to cells C34 and AD34 we see that 1.76 mg/L carbonate ion is converted to bicarbonate ion (and possible subsequently to carbonic acid):



Cells C33 and AD33 show bicarbonate being reduced from 179.25 mg/L to 85.56 mg/L while C32 and AD32 show carbonic increasing from 2.07 to 99.02 mg/L and this

carbonic clearly comes from conversion of bicarbonate (which was, perhaps originally carbonate) by the second reaction (first arrow below):



The third reaction, shown by the second arrow, is the conversion of carbonic acid to carbon dioxide gas and water. Thus it is clear that the bicarbonate that enters into this reaction is replaced by (in the case of hydrochloric acid) chloride ion.

To see how much acid is required to get to pH 6.3, how much of the carbo will be removed by this acid treatment and how much chloride ion will be left behind we use the synthesis portion of the spreadsheet. Make sure that all entries in (J:W,22) are set to 0, then increment S22 (for *HCl*) until the proton deficit in Z35 shows 0, or let the Solver do this. Proton deficit will be 0 when 58.12 mg (Cell S22), equivalent to 0.13 mL of 23 Baume acid, is added to each liter of water. This value will be displayed in S71 if the total volume to be treated is set to -1 in Cell J70 indicating 1 liter total volume to be treated. To find out the amount of acid of this strength required to treat 5 gallons enter +5 in J70 and read 2.43 mL in Cell S74).

Cell W38 shows that this *HCl* adds 56.5161 mg/L chloride ion to the water. Copy this number into cell AD38 in the Target Area and (AE,53:55) will show electrical balance of 0.

As  $\text{CO}_2$  escapes the solution (and it will as AB70 shows that 0.04 atm partial pressure of  $\text{CO}_2$  would be required to keep it in solution) the pH will rise. Note that the hydrochloric acid we added is consumed in the reaction, forming carbonic acid which decomposes into carbon dioxide and water, i.e. there are no hydrogen ions from this source left to hold the pH down. Let us assume that of the 55% of carbo that was converted to  $\text{CO}_2$ , most escaped, so that the total carbo content is 1.5 instead of 3 as at the outset. To see what the effect of loss of this much  $\text{CO}_2$  would be set AB21 to 1.5 and vary the pH in cell AD3 until electrical balance is achieved. pH 7.505 is the value which gives 0 balance and this then is the theoretical pH to which water with the properties in the Souce Area would come if 58.12 mg *HCl* were added per liter and half the carbo escaped as  $\text{CO}_2$ . Note that Cell AB70 shows that the water is over saturated with respect to  $\text{CO}_2$  as the equilibrium pressure at 0.0025 atm is almost an order of magnitude greater than the atmospheric partial pressure of this gas which is 0.0003 atm. Having lost half its carbo this water would thus continue to lose  $\text{CO}_2$  until the equilibrium pressure in AB70 reaches 0.0003. To se what the water would look like under these conditions we ask the Solver to vary pH (AD3) and carbo (AB22) to set electrical imbalance (AE54) to 0 subject to the constraint that the equilibrium pressure (AB70) be 0.0003 atm. Solver finds a solution with pH equal 8.402, total carbo 1.40 mmol/L with 83.33 mg  $\text{HCO}_3^-$  Compared to 179.25 in the original water (C33) this represents a loss of 95.92 mg/L or 1.57 mEq/L. The sodium levels are the same in the treated and untreated water but the missing 1.57 mEq/L bicarbonate has been replaced by. Note that the missing  $\text{HCO}_3^-$  has been replaced by

1.59 mEq/L chloride and the pH has wound up slightly higher at 8.42 but that is because we have allowed the treated water to go to equilibrium with the air whereas the original water was not at equilibrium (see Cell C70). If we let the treated water lose  $CO_2$  only to the point where the original pH (8.3) is restored (set the pH in AD3 to 8.3 and then ask the Solver to zero AE54 by twiddling carbo without any constraint on the partial pressure of  $CO_2$ ) we find that the resulting bicarbonate concentration is at 83.88 representing a loss of 1.56 mEq/L but that the equilibrium  $CO_2$  pressure is only 0.0004. This is so close to 0.0003 that it will take a long time for the remaining small amount of  $CO_2$  to escape.

To summarize this last section: when acid is added to carbonaceous water the carbonate and bicarbonate are converted to carbon dioxide gas which escapes the solution. When allowed to come close to equilibrium with air  $CO_2$  we find that the bicarbonate removed is replaced, approximately, equivalent for equivalent, with the anion of the acid used (e.g. chloride, sulfate). Thus when we used hydrochloric acid in this example, we replaced almost 1.6 mEq/L bicarbonate with almost 1.6 mEq/L chloride ion. Had we used sulfuric acid to remove the same amount of bicarbonate we would replace it with almost 1.6 mEq/L sulfate ion.

Clearly decarbonation by use of acid is not the proper method to use when it is desired to keep the ion content of the water low as for Bohemian Pils or other beers that are brewed with water of low ion content.

**Alkalinity Check:** Alkalinity should be checked before and after any decarbonation treatment to measure treatment success. This is easily done with a simple test kit such as Hach's AL-AP MG-L (\$37.89, [www.hach.com](http://www.hach.com)) or a similar, and perhaps less expensive, kit from an aquarium supply store (Red Sea Alkalinity Pro Test Lab, \$13.99, [www.thatpetplace.com/pet/prod/240704/product.web](http://www.thatpetplace.com/pet/prod/240704/product.web)).

Generally one should be able to decarbonate down to an alkalinity of about 50 ppm as  $CaCO_3$  or 1 mEq/L (mval). With additional calcium it may be possible to go even lower. Note that each unit of alkalinity reduction by this method results in a reduction of calcium hardness by an equal amount (in mEq/L or ppm as  $CaCO_3$ ). Thus one often supplements calcium to make up for this loss. If you are planning to do this, do it before the lime or heat treatment to get the Le Chatelier benefit.

## Appendix E: Hardness

As noted in the body of this document hardness refers to the concentration of calcium and magnesium in a water sample. Measurement of calcium and magnesium is usually accomplished by a simple titration and it is this titration that we will be describing here.

As with alkalinity, a 100 mL sample is usually drawn and placed in a suitably sized flask. A buffer is added to bring the pH to a level where the indicators employed show the

sharpest “end points”. In this case the end point is the point at which all calcium and magnesium is removed from the solution. Eriochrome Black-T is an example of an indicator. Its complex with calcium or magnesium (or as we noted in the body, with some other metals) is wine red but if no metals are present it is a pale blue. A small amount of the indicator is placed in the flask with the buffered sample and then a chelating agent<sup>18</sup>, usually Ethylene Di-amine Tetra Acetic Acid (EDTA) is added in small increments (titration) while the color is monitored. When sufficient chelant to capture all the calcium and magnesium ions has been added the solution changes color from red to blue. The strength of the EDTA is known and from the strength and amount of solution used to accomplish the color change one can calculate the amount of calcium plus magnesium in the solution. This is called the *total hardness* and is usually expressed in units of ppm as calcium carbonate but can be expressed in mEq/L (mval). There are also several other units that may be encountered such as grains per gallon, French degrees, German degrees etc.

If it is desired to know separately the amounts of calcium and magnesium (and, for brewing it is) then the titration can be done in two steps in the first of which the magnesium is removed from the solution before the titration begins. This is accomplished by adding a buffer at a pH high enough that magnesium hydroxide gel forms and precipitates. A titration carried out at this pH responds only to the calcium in the water as it stays in solution. A different indicator, which performs better at this higher pH may be used. The magnesium hardness is obtained by subtracting the calcium hardness as obtained from the procedure just described from the total hardness measured as described earlier.

Hach company (see above under alkalinity) and others sell an assortment of kits suitable for measuring hardness. They vary in cost, range and precision.

## Appendix D: Phosphate

**Contribution to Alkalinity:** Where phosphate (or any other polyprotic acid or its salts) is involved, there is a distribution of species calculated in exactly the same fashion as for carbo, except that if there are more than 2 protons (as there are with phosphate and citrate) there will be more than 2 *r*'s and 3 *f*'s. These species will contribute to alkalinity in exactly the same way that carbo species do. For an acid that carries *n* protons, the dissociation of the *j*th is described by the ratio

$$r_j = 10^{(pH - pK - (2j-1)pf_m)}$$

The fraction that is in un-dissociated acid is

---

<sup>18</sup> From the Greek “chela”, a claw, i.e. a substance that “grabs” a metal, here calcium and magnesium, thus rendering it unavailable to react with other substances (in particular the indicator).

$$f_1 = \frac{1}{1 + \sum_{j=1}^n \prod_{k=1}^j r_k}$$

and the fraction that has lost  $m$  protons is

$$f_{m+1} = r_m f_m.$$

At a given pH the total number of protons in this system (e.g. the phosphate system) is

$$n_p = P_T \sum_{j=1}^{n+1} (n-j+1) f_j$$

which is, using phosphate as an example, three times the number of moles ( $P_T$  would be the total moles of  $(PO_4)$  in this example) that are in the acid, plus twice the number of moles in monobasic phosphate, plus the number of moles that are in dibasic phosphate.

In going from a higher pH (sample) to a lower end point pH where more moles are in the highly protonated states, the amount of acid required to get to the end point would be

$$alk_P = P_T \sum_{j=1}^{n+1} (n-j+1) (f_{j,e} - f_{j,i})$$

and this, of course, will show up as an additional (beyond carbonate) alkalinity.

**Saturation:** Just as a solution is subject to saturation with respect to calcium carbonate, it can also be saturated with respect to hydroxyl apatite,  $Ca_{10}(PO_4)_6(OH)_2$ , as this substance (the material of bone and teeth) is of very limited solubility, with the constant in the governing equation

$$\{Ca^{++}\}^{10} \{PO_4^{-3}\}^6 \{OH^{-}\}^2 = K_{sp}$$

having a value corresponding to  $pK_{sp} = 114$ . The activity of the phosphate ion can be written as

$$\{PO_4^{-3}\} = \frac{K_{3p} \{HPO_4^{-2}\}}{\{H^+\}}$$

and that of hydroxyl as

$$\{OH^{-}\} = \frac{pK_w}{\{H^{+}\}},$$

with  $pK_{3p}$  being the 3<sup>rd</sup> dissociation constant of phosphate and  $pK_w$  being that of water.

Substituting gives

$$\frac{\{Ca^{++}\}^{10} \{HPO_4^{-2}\}^6 K_{3p}^6 K_w^2}{\{H^{+}\}^8} = K_{sp}$$

Applying the  $p$  operator to this equation and simultaneously replacing each ion's activity (with the exception of hydrogen's) by the product of the molar concentration, the square of the ionic charge and the average ionic activity, we have

$$64p_{f_m} + 10p[Ca^{++}] + 6p[HPO_4^{-2}] + 6pK_{3p} + 2pK_w - 8pH - pK_{sp} = 0$$

as the calcium phosphate saturation condition, where  $p_{f_m}$  represents minus the log of the average, single-charged, ion activity. This can be readily solved to determine the maximum concentration of calcium at the given pH and dibasic phosphate concentration

$$p[Ca^{+2}] = 0.1pK_{sp} + 0.8pH - 0.2pK_w - 0.6pK_{3p} - 0.6p[HPO_4^{-2}] - 6.4p_{f_m}$$

or for the pH at which the solution, with given levels of calcium and dibasic phosphate, would be saturated

$$pH_s = 8p_{f_m} + 1.25p[Ca^{++}] + 0.75p[HPO_4^{-2}] + 0.75pK_{3p} + 0.25pK_w - .125pK_{sp}$$

For a given amount of phosphate in a system  $[HPO_4^{-2}]$  depends on the pH, so the pH as calculated above can not be interpreted as the pH to which the system would have to be taken in order to bring it to saturation. The interpretation is, rather, that if  $pH_s < pH$  the solution is saturated at  $pH$ , and, conversely, if  $pH < pH_s$  it is undersaturated.

## References

1. deLange, A.J. "Alkalinity, Hardness, Residual Alkalinity and Malt Phosphate: Factors in the Establishment of Mash pH" *Cerevesia*, 29(4) 2004 pp188-198. Available at [www.wetnewf.org](http://www.wetnewf.org)

2. Kolbach, Paul “Der Einfluss des Brauwassers auf das pH von Würze und Bier”, Wissenschaftliches Beilage Monatsschrift für Brauer 6 Jahrgang Nummer 5 Mai 1953. English translation available at [www.wetnewf.org](http://www.wetnewf.org)
3. deLange, A.J. “Deconstructing Water Residual Alkalinity and Mash pH”, The New Brewer, July/August 2003.
4. deLange, A.J. “Understanding Alkalinity and Hardness – Part I”, unpublished. Available at [www.wetnewf.org](http://www.wetnewf.org).
5. deLange, A.J. “Understanding Alkalinity and Hardness – Part II”, unpublished. Available at [www.wetnewf.org](http://www.wetnewf.org).
6. Eaton, Andrew D., L. S. Clesceri, A.E. Greenberg, Ed. “Standard Methods for the Analysis of Water and Wastewater, 19<sup>th</sup> (or any subsequent) Edition, APHA, AWWA, WEF, Washington, DC 1995.
7. Stumm, Werner, and J. Morgan, “Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters” Wiley, New York, 1981.
8. Hardwick, William A. Ed., “Handbook of Brewing”, Marcel Dekker, New York, 1994: Chapter 8 “Water” by M. M. Moll.
9. Briggs, D.E., J. S. Hough, R. Stevens, T. W. Young “Malting and Brewing Science Second Edition”, Chapman and Hall, London 1981 Vol I p 90