Understanding Alkalinity and Hardness - Part I

1.0 INTRODUCTION

In a recent Brewing Techniques article (Ref 1.)I discussed chlorine and chloramine in brewing water. The total chlorine concentration in a sample of brewing water is one of what I call the *significant seven* water characterization parameters because given that a brewer has values for these he has a quite complete picture of how his water will perform in the mash tun and what characteristics it will impart to the finished beer. The complete list of significant 7 parameters looks like:

1. pH
2. Alkalinity
3. Calcium Hardness
4. Magnesium Hardness
5. Chloride Ion (not chlorine) concentration
6. Sulfate Ion concentration
7. Total chlorine (not chloride) concentration

pH was the subject of two other BT articles (Refs 2. and 3.) Since I have written about two of the seven in these pages it seems to make sense to continue with the other 5 and I propose to do that in a series of 3 articles of which this is the first. As alkalinity and hardness are intimately related and are at the heart of brewing water chemistry I will discuss them together but will need two installments to do it in as there is quite a bit to cover. A third installment will deal primarily with chloride and sulfate but will also touch on trace metals such as iron, manganese, zinc and copper which can be problematical with some brewing waters. I will give a definition of each parameter, show how home (and commercial) brewers can measure it using inexpensive kits, describe its significance in brewing, and present means of reducing and increasing its value as may be required for particular beer styles.

This first part contains the core of brewing water chemistry and is definitely the most difficult. I have tried to keep the technical details to a minimum. More detail on many of them are to be found in Ref. 2. At the same time Ref 4. serves as an excellent introduction to much of what I will be discusing here in a bit more depth.

2.0 ALKALINITY

Alkalinity is perhaps the most significant of water parameters because it is alkalinity which determines the pH of the mash and the pH of the mash in turn has a dramatic effect on several phases of the brewing process. These were enumerated in Ref 2. When the alkalinity of the brewing water is not balanced by malt acidity, the brewer must make adjustments or the pH of the mash will be outside the desired range. Imbalance can be in either direction. A very alkaline water has more alkalinity than can be balanced by the acids produced by a pale malt and the resulting mash pH will be too high. Conversely, a grist containing a large proportion of dark malt will liberate more acid than can be neutralized by dough-in water of low alkalinity and pH lower than desired will result. Methods of adjustment of mash pH will be discussed in Part II of this article.

2.1   Definition of Alkalinity

Most brewers remember from high school or college chemistry that "alkali" is another name for a chemical base, that a base is the opposite of an acid and that acids and bases neutralize each other. Alkalinity is indeed a measure of the amount of base in a sample of brewing water. It is the amount of acid required to neutralize the base in a sample of the water under investigation. It is also a measure of the water's *buffering capacity* (see Ref. 2.)

If the water is suitable for brewing, the base it contains is composed almost exclusively of bicarbonate (HCO_3^-) ions with a smaller number of carbonate (CO_3^{-2}) ions. The relative number depends upon the pH and, to a lesser extent, the temperature. Given the pH we can easily compute carbonate and bicarbonate ion concentrations from alkalinity or, given the pH and the concentration of either carbonate or bicarbonate calculate the concentration of the other and the alkalinity (see sidebar). Because it will help both in understanding of the defintion of alkalinity and the relationship of bicarbonate and carbonate concentration in brewing water (and mash) we'll digress for a bit into the chemistry of carbonates which is the heart of the chemistry of brewing water.

2.2   Introduction to the Chemistry of Carbonates

Acids are (by one definition) substances which when added to water liberate hydrogen ions. Strong acids, such as hydrochloric acid and sulfuric acid, are acids for which this dissociation process is complete i.e. they liberate all their hydrogen ions (and an anion such as sulfate ion if the strong acid is sulfuric, chloride ion when it is hydrochloric, etc.). Weak acids do not release all their hydrogen ions. More on strong acid and weak acids can be found in Ref. 2. Strong acid is used in measurement of alkalinity.

If acid, strong or weak, is added to a solution containing bicarbonate ions, HCO_3^-, hydrogen ions, H^+, will react with the bicarbonate as follows:

$$H^+ + HCO_3^- \quad H_2CO_3 \tag{2.1}$$

The species on the right hand side, H_2CO_3, is carbonic acid. The double headed arrow indicates that the reaction does not go to completion meaning that at the same time hydrogen ions are combining with bicarbonate ions to form carbonic acid molecules, carbonic acid molecules are decomposing into bicarbonate ions and hydrogen ions. At equilibrium there will be hydrogen ions, bicarbonate ions and carbonic acid molecules simultaneously present in the solution. Note that the carbonic acid may also decompose into carbon dioxide gas and water. While this is not significant to the current discussion it is an important part of the mechanism by which boiling causes precipitation of carbonates. This will be discussed in Part II.

If the solution contains carbonate ions the presence of hydrogen ions will cause some to convert (again the amount depends upon temperature and pH) to bicarbonate:

$$H^+ + CO_3^{-2} \quad HCO_3^- \tag{2.2}$$

This bicarbonate can, in turn, react with another hydrogen ion per Equation (2.1) to form carbonic acid. See Ref. 2. for more detail on reactions like those of Equations (2.1) and (2.2).

We can put these two chemical reactions together into a diagram like that on the bottom of Figure 2.1. Beginning at the far right we have carbonate ions CO_3^{-2}. Moving to the left we have hydrogen ions, H^+, coming in to produce, in the middle of the diagram, bicarbonate, HCO_3^- ions and moving still further to the left, with the addition of more hydrogen ions, we come to carbonic acid, H_2CO_3. Each of the three species is placed on the diagram near the value on the graph's pH scale where that particular species' concentration is highest. Thus carbonic acid is most prevalent at low pH, bicarbonate is most prevalent at a pH of 8.4 and carbonate is most prevalent at high pH. The curves on the graph shows the relative percentage of each of the species at each pH. I collectively refer to the three species, *carbo*nic, *carbo*nate and bi*carbo*nate as the *carbo species*. At pH below 4.3, more than 99% of the carbo species are carbonic. At pH 8.4 about 98% of the carbo species are bicarbonate and the fractions of carbonate and carbonic are equal at approximately 1.2%. At hgher pH i.e. above 10.4 carbonate is the most prevalent. It is rare that the brewer will encounter pH above 8.5 in his water supply because current drinking water standards dictate that public water supplies should not excede this pH value. Brewers do, however, adjust their water's pH to levels where carbonate predominates in order to precipitate it as the calcium salt. This will be discussed in Part II.
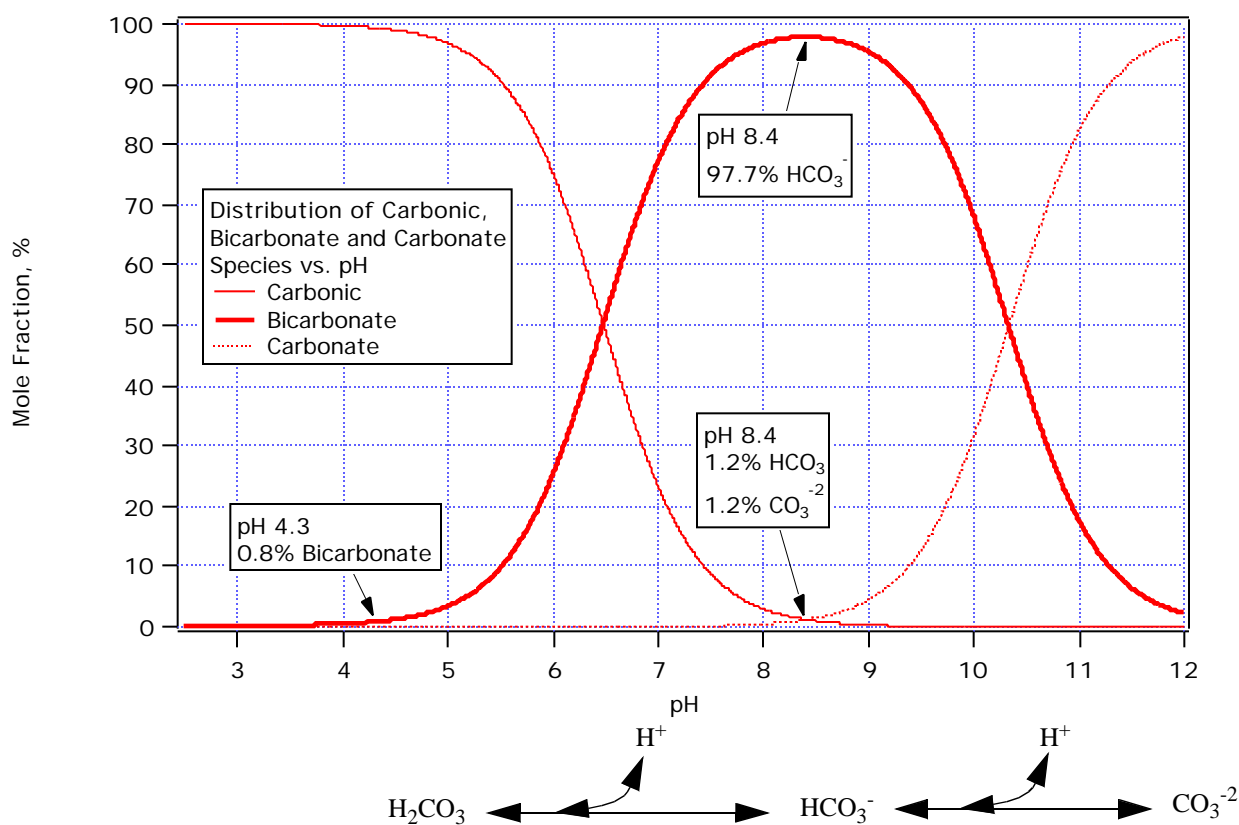

Figure 2.1   Relationships between pH and concentration of carbo species

The arrows in Figure 2.1 are double headed meaning that one can, by supplying or taking up hydrogen ions, move in either direction establishing the relative amounts of the three carbo species as desired. By adding hydrogen ions in the form of acid we move towards the left of the diagram, lowering pH and increasing carbonic at the expense of bicarbonate and bicarbonate at the expense of carbonate. Similarly, by adding base, we increase pH forcing carbonic to convert to bicarbonate yielding up hydrogen ions in the process. Increased pH also forces bicarbonate to convert to carbonate and this also yields hydrogen ion[1].Freed hydrogen ions combine with hydroxyl ions, $(OH)^-$, from the base (one definition of a base is something which releases hydroxyl ions) to form water.

2.3   Units of Measurement

At this point we must discuss the units in which the concentrations of chemical species are measured. The remarks that follow apply not only to alkalinity but to hardness and the concentrations of other ions (such as chloride and sulfate).

2.3.1   The Mole - Molecular Weight

The most fundamental unit of quantity in chemistry is the *mole*. A mole is 6.02 x 10^{23} objects, a huge number called *Avogadro's number*. The mole is handy because we can simply calculate the weight of a given number of moles of something by multiplying by the *molecular weight* which is the weight of a mole of the substance in question. Values for molecular weight are tabulated in various chemical handbooks. The *gram molecular weight* is by far the most common form of the molecular weight and, as the name suggests, gives the weight of a mole in grams. For example, a mole of carbonic acid weighs 62 grams, a mole of bicarbonate ion weighs 61 grams and a mole of carbonate ion weighs 60 grams. Note that in Figure 2.1 the vertical axis is labeled "mole fraction". If we count all the carbonic acid molecules in a volume of water, add the number of bicarbonate ions and the number of carbonate ions and divide the sum by Avogadro's number we would have the number of moles of carbo species in the sample. Multiplying that number by the fraction which is carbonic acid gives the moles of carbonic acid and multiplying that by 62 gives the weight of carbonic acid in the sample volume. The same can be done for the other two carbo species.

The term *atomic weight* refers to the weight of one mole of atoms. We don't usually deal with atoms in water chemistry but we do deal with ions which, in some cases (calcium, sodium, potassium, chloride etc) are atoms which have lost or gained an electron or two. The electron's mass is very small compared to the rest of the atom so the atomic weight for the element applies to the ion as well. I will use the term molecular weight even when discussing ions. The reader may simply think of the ion as a molecule containing only a single atom (plus or minus the electrons).

Example: A sample contains carbo species to the extent of 2 millimoles per liter (abbreviated mM/L - a millimole is one thousandth of a mole and is the unit we will use in nearly all water chemistry work) and is at pH 8.4. What are the molar concentrations and concentrations by weight of the three carbo species?

[1.] This implies that bicarbonate ions are acidic but they are also basic because they can take up hydrogen ions in becoming carbonic acid. Ions with this dual nature are said to be *amphoteric*.

Solution: From Figure 2.1 the mole fractions of carbonate and carbonic are each 1.2%. As the total carbo molar concentration is 2 mM/L the concentration of each of the two se is 0.024 mM/L. With carbonic having a molecular weight of 62 grams per mole (62 milligrams per millimole) the concentration of this species is approximately 1.5 milligrams per liter (mg/L). For carbonate the molecular weight is 60 and thus the concentration in mg/L is about 1.4 mg/L. The mole fraction of bicarbonate at pH 8.4 is about 97.7% (the total percentage is not quite equal to 100 because the numbers on the figure have been rounded to 1 decimal place) so the molar concentration is 1.954 mM/L. With its molecular weight of 61 the bicarbonate concentration in this sample is thus 119.2 mg/L.

2.3.2 ppm and mg/L

In the preceding example we calculated the number of milligrams of bicarbonate ions in a liter of solution. mg/L are common units for expression of substance concentration in brewing water. As the weight of dissolved substance in virtually all water chemistry problems is, in common with this example, very small compared to the mass of the water it is dissolved in we can generally assume that the addition of the substance to the water does not appreciably change the volume of the water. Thus the amount of ion per liter of solution is very close to the amount of ion per liter of water. As a liter of water weights a killogram (1000 grams), 1 mg (0.001 gram) of substance dissolved in it amounts to 1 part per million abbreviated ppm. This approximation is only valid for dilute solutions which brewing water samples tend to be. Compare to the solutions of wort we make when we dissolve sugars to the extent of 10 to 20% of the total wort weight. These solutions are not dilute and we require tables like the Brix tables to give us the relationships between volume based and weight based concentrations.

In dealing with brewing water chemistry ppm and mg/L are often used interchangably and this is justified.

2.3.3 The Equivalent and the Val - Equivalent Weight

When the species being quantified are charged, as are the ions we are interested in, chemists often quantify them in terms of the number of moles of electric charge. One mole of electric charge is called an *equivalent* (because a number of equivalents of plus charges reacts with an equal number of negative charges). Because of the dilute nature of brewing waters, we usually specify charge in milliequivalents (thousandths of an equivalent).Charges on ions are often associated with *val*ences which represent the ability to form chemical bonds. From this teminology we get the *val* which is the same as an equivalent. I mention vals, because this unit (or more usually millivals - mval) are frequently used in brewing literature, particularly that of European origin.Whether milliequivalents or millivals are used concentrations are always, of course per liter i.e. milliequivalents/Liter (mEq/L) or millivals per liter (mval/L). In many texts the "per liter" part is omitted when millivals are being used i.e. one sees just mval. Where it is obvious that concentration is meant the reader must supply the "per liter" i.e. 1 mval is equal to 1 mEq/L. I will use mEq/L in these articles.

If an ion bears a single positive or negative charge (as does bicarbonate) its molar concentration (called its *molarity*) and its equivalent concentration (called its *normality*) are the same because 1 mole of the ion carries 1 mole of charge. If the ion carries a double charge (as do carbonate, calcium and magnesium, for example) its normality is twice its molarity. Just as there is a molecular weight which gives the weight of one mole of a species, there is an *equivalent weight* which gives the weight of the amount of the species which carries one mole of charge. If an ion carries a single charge its molecular weight and equivalent weights are the same. If it carries a double charge its equivalent weight is half its molecular weight. Thus, for example, the equivalent weight of carbonate ion is 30 mg/mEq while its molecular weight is 60 mg/mM.

2.3.4   As $CaCO_3$

Unfortunately an accepted practice in the water industry specifies both alkalinity and hardness in units of *ppm as calcium carbonate* or *mg/L as calcium carbonate*. Many people wind up confused by this. Some situations which lead to confusion are:

- If a brewer puts 100 milligrams of calcium carbonate in a flask and adds a liter of water, it won't dissolve. If he adds enough hydrochloric acid to the water to get the chalk to dissolve and bring the pH to a value less than 8.4 the alkalinity of the water will be less than 50 mg/L as $CaCO_3$ with the actual value dependent on the pH. If, on the other hand, he bubbles enough CO_2 through the water to get the chalk to dissolve the alkalinity, as $CaCO_3$, will be approximately equal to 100 ppm regardless of the final pH (even if it is greater than 8.4).

- So called "permanent hardness" (see Section 3.1) is attributable partly to magnesium and partly to sulfate and chloride ions (i.e. no carbonate) and yet is often reported "as calcium carbonate"

- Magnesium hardness has nothing to do with calcium and may be partially attributable to chloride and sulfate yet is quantified "as calcium carbonate".

- A sample containing only magnesium sulfate would have a finite hardness "as calcium carbonate" even though it contains no calcium and no carbonate.

- Most water samples contain very little if any carbonate - most of it has been converted to bicarbonate.

- There is an erroneous definition of what "as calcium carbonate" means abroad. It is used in some popular brewing books and magazine articles. One alkalinity test kit I tested reports its result based on this erroneous definition.

The concentration of an ion "as $CaCO_3$" is 50 times its normality (concentration in mEq/L or mEq/L). Thus "as $CaCO_3$" is just another way of expressing the normality . That's all there is to it and you'll have a much better time of it if you think of it simply in these terms without searching for additional meaning. Looking at the magnesium hardness as an example, if your water report tells you that your magnesium hardness is 25 ppm as $CaCO_3$ don't ask yourself what calcium carbonate has to do with magnesium. Just divide by 50 to convert your magnesium hardness to 0.5 mEq/L. Then multiply by the equivalent weight of magnesium (12.15) to see that you have about 6 mg/L of magnesium ions in your water.

I mentioned that there is an erroneous definition in use. In this definition the normality is multiplied by 100 rather than 50. The value selected is arbitrary so why do I use 50? In most industries there are accepted analytical standards designed to prevent confusion of this sort from occuring. In American brewing the standards authority is the American Society of Brewing Chemists and their "Methods of Analysis" (Ref 5.) prescribes the accepted methods for analysis of beer and its constituent ingredients. Water is an exception. Analysis of water requires a set of standards even more extensive than Ref 5. and these are, as you might expect, promulgated by a body made up of various groups associated with the water industry, in particular the American Public Health Association, the American Water Works Association and the Water Environment foundation. Their analystical standards are published as "Standard Methods for the Examination of Water and Wastewater" (Ref. 6.). Rather than reinvent the wheel, the ASBC, simply accepted Ref. 6. and incorporated it by reference into Ref 5. The factor 50 is taken from Ref. 6. and is, at least by the preceding argument, the proper value to use in brewing. There is, of course, a reason why the value of 50 was chosen and that relates to the first part of the first bullet in the areas of confusion listing at the beginning of this section. If x grams of calcium carbonate (limestone and chalk are natural forms of CaCO3) are dissolved by water containing carbonic acid (dissolved carbon dioxide) the alkalinity of such water will be about x ppm as CaCO3 regardless of its pH. Thus the alkalinity in mg/L as calcium carbonate reflects the amount of limestone dissolved by subsurface water acidified by CO_2. The major source of calcium carbonate is most brewing water is of course exactly that.

Let's return to the example of Section 2.3.1 where we had 1.954 mM/L bicarbonate. This is 1.954 mEq/L because bicarbonate has a single charge. Multiplying by 50 gives us 97.7 mg/L (or ppm) as $CaCO_3$. This same sample had 0.024 mM/L carbonate which, as carbonate is a doubly charged ion, is 0.048 mEq/L. Multiplying this by 50 gives 2.4 mg/L as CaCO3. Jumping ahead a little, the sum of these two values is approximately 100 which, as we shall see shortly, is the alkalinity of this water sample.

2.3.5 Other Units

Readers will occasionally encounter other units for measuring hardness and alkalinity. All are based on eqivalence (as is "as $CaCO_3$"). In the USA *grains per gallon* is still fairly common. One grain per gallon is 0.342 mEq/L and thus 17.1 mg/L as $CaCO_3$. In European brewing literature the *German degree* (dH) is often used. One dH is 0.3574 mEq/L and thus equal to 17.87 ppm as $CaCO_3$. One *French degree* is 0.2 mEq/L (10 ppm as CaCO3) and one *English degree* is 0.285 mEq/L or 14.25 ppm.

2.4 Formal Definition of Alkalinity

Alkalinity is formally, and quite simply, defined as the number of milliequivalents of strong acid required to bring 1 liter of the water sample to pH 4.3. The mEq/L value is, in most cases, multiplied by 50 to convert the value to "as CaCO3". Alkalinity is thus a measure of the *buffering capacity* of the water which is its ability to resist pH change when acid or base is added (see Ref. 2.).

Reference to Figure 2.1 shows that at pH 4.3 all but 0.7% of the bicarbonate and all the carbonate have been converted to carbonic. Each carbonate ion requires two hydrogen ions (one to convert it to bicarbonate and one to convert the bicarbonate to carbonic) and each bicarbonate ion requires one hydrogen ion to convert it to carboninc. Put another way, each mole of bicarbonate ion requires 1 mole of hydrogen ions and each mole of carbonate two. Put yet another way each equivalent of bicarbonate ions requires 1 equivalent of hydrogen ions and each equivalent of bicarbonate also requires one of hydrogen ions to reach this pH. As equivalents and moles of hydrogen ions are the same (the hydrogen ion is singly charged) the alkalinity of a sample is (ignoring the 0.7% not converted) the number of mM/L of bicarbonate in the sample plus twice the number of mM/L of carbonate or the sum of the mEq/L bicarbonate and the mEq/L carbonate. Thus the example water sample of Section 2.3.1 has alkalinity of 100 as calculated in Section 2.3.4.

The definition of alkalinity is arbitrary in that we have selected pH 4.3 as our *end point* i.e the value of pH at which we stop adding acid and see how much we have used. Why not pick 4.5 or 3.8? Unfortuantely Ref. 6. does not specify an end point but rather leaves the choice (guidelines on how to pick one are given) of end point to the analyst requiring only that he specify the value of the end point he used. If this is done one can use the formulas like those in the side bar (Section 5.0) or the curves of Figure 2.1 to obtain a complete and accurate picture but it is much simpler to follow Moll (Ref. 7.) and always use an end point of 4.3. This choice under estimates alkalinity by requiring that enough acid be added to convert 99.2% of the bicarbonate to carbonic. At the same time it over estimates the alkalinity by 2.5 ppm as $CaCO_3$ because even if the water contained no dissolved carbo species that much acid would be required to establish a pH of 4.3. These over and underestimations tend to cancel each other out to some extent. Exact cancellation is possible if the end point pH is chosen correctly, based on a reasonable a priori estimate of the alkalinity. This is the basis for the end point pH recomendations of Ref. 6. This detail can be ignored for brewing work.,

2.4.1   P Alkalinity and M Alkalinity

Brewers will sometimes see references to "P alkalinity" and "M alkalinity". M alkalinity is the alkalinity we have discussed thus far and it is sometimes called "total alkalinity". The "M" stands for "methyl orange", an idicator dye which changes color near pH 4.3, the end point pH of our definition. The "P" in P alkalinity stands for phenolpthalein, another indicator which turns color at about pH 8.3. When testing samples with pH greater than 8.3 the amount of titrant required to reduce pH to 8.3 is sometimes noted. This value is the P alkalinity value and rough conclusions concerning the relative amounts of cabonate, bicarbonate and hydroxide can be drawn by comparing the P and M alkalinities. As brewers should not encounter water with pH much higher than 8.3 and as hydroxide alkalinity should not be present to any appreciable extent, I will not discuss P alkalinity further. I've only mentioned it because most kits test for it. Further details can be had from Ref 6. or 9.

2.5   <u>Measuring Alkalinity</u>

The definition of alkalinity makes it pretty clear how it is to be measured. A sample of water is placed in a suitable container and acid is added to it in measured increments until the end point pH is reached. There are many ways to do this which differ in how the end point pH is sensed and how the acid is metered. *Titration* is the name given to the gradual metering process and the substance being metered, in this case strong acid of known strength, is called the *titrant*. The *end point* is, as the name suggests, the point (pH) at which the titration is ended and the amount of acid used read from the metering device. The metering device can be a conventional buret, a modern digital buret, a dropper bottle or a hypodermic syringe. The end point is usually determined in the laboratory by means of a pH meter and in the field or small brewery by means of an indicator dye. These are organic compounds which change color as pH changes. In alkalinity measurement the usual indicator is a mixture of brom-cresol green and methyl red. It transitions from light greenish blue-gray at pH 5.1 to light pink at pH 4.5.

Typical test kits are exemplified by the Hach Model AL-AP MG-L, Catalog 24443-01 (0 - 400 mg/L as CaCO$_3$) illustrated in Figure 2.3 (middle). This kit contains a small bottle (about 30 mL capacity), a small measuring cylinder, two indicators (phenolpthalein and bromcresol-green/methyl-red) and a dropper bottle of sulfuric acid. If the alkalinity is high (over, say, 100 mg/L as CaCO$_3$) the small cylinder is filled (about 3.3 mL) with the sample water and emptied into the test bottle. A small pouch of phenolphthalein is added and mixed and then drops of sulfuric acid are added one at a time until the red phenolphthalein turns clear. This step can be skipped in the brewing application as the P-alkalinity measurement is not needed and the pH of most brewing waters will be less than 8.3. Next, a small pouch of bromcresol-green/methyl-red is added and drops of sulfuric acid titrated in until the color changes to blue-green. The total alkalinity is 20 times the number of drops used.

If the alkalinity is thought to be below 100 or so mg/L as CaCO$_3$ the procedure is exactly the same except that the test bottle is filled to the 23 mL mark (4 times the amount in the high range test). Each drop of sulfuric acid used then corresponds to 5 mg/L as CaCO$_3$.

More accurate results can be obtained by using a conventional buret though these are not very popular any more having been replaced by the more convenient digital buret. A conventional buret consists of a long, graduated cylinder with a stopcock at the lower end. To use one these the analyst carefully (disturbance which would cause CO$_2$ gas to escape the sample is to be avoided) measures 100 mL of the sample into a clean beaker, places it on a stir plate (set for a slow stir), adds a stir bar and a small amount of bromcresol-green/methyl-red or lowers a calibrated pH meter electrode into the beaker. He fills the buret with 0.1N hydrochloric acid (this means that each mL of the acid contains 0.1 mEq of hydrogen ions). By operating the stopcock he titrates until pH 4.3 is reached either as indicated by a color change in the indicator or the pH meter. The alkalinity, in mEq/L is the number of mL of acid. This number is multiplied by 50 to get the alkalinity in ppm as calcium carbonate (as CaCO$_3$). The sample size or the strength of the titrant is adjusted according to the expected alkalinity so that enough acid will be used that the buret can be read accurately. If, for example, the alkalinity is around 100 the 100 mL sample size and 0.1 N acid would require 2 mL of acid to be used. To increase the precision of the test, 0.02 N acid might be used instead of 0.1N. In this case 10 mL of acid would be required and a 0.1 mL error in reading the buret would lead to a 1% error rather than a 5% error as would be the case where the end point is reached with 2 mL. For high levels of alkalinity the size of the sample can be reduced. By changing the strength of the titrant and volume of sample a wide range of alkalinities can be measured. A general formula for the measured alkalinity (from Ref 6.) is

$$Alk = \frac{50000AN}{V} \qquad (2.3)$$

where the alkalinity is in mg/L (ppm) as CaCO$_3$, A is the mL of titrant used in reaching the end point, V is the normality of the titrant and V is the sample volume in mL. Note that when high alkalinity dictates a small sample volume the sample can be diluted with deionized water to a volume more convenient to work with without changing the accuracy. In this case V is the sample volume before dilution.

The titration is made much simpler and its accuracy and convenience are improved by the use of a *digital buret* illustrated in Figure 2.2. This is a patented device, made by the Hach Company (Cat no. 16900-01) which accepts titrant cartridges which are very much like hypodermic syringes without the needle or plunger handle (the plunger tip is there). The cartridge goes into an appliance which advances the plunger tip with a lead screw connected to a counter like the odometer in an automobile. Instead of a needle, the tip of the syringe is fitted with a small diameter polyethylene dip tube. The sample is placed in a beaker or flask and the indicator or pH meter electrode added. The digital titrator dip tube tip is placed beneath the surface of the sample and titrant ejected from the cartridge by turning a knob which rotates the lead screw and advances the plunger tip. At end point the odometer-like dial is read directly in units of alkalinity. Dilution and choice of titration cartridge, which come in several strengths, make operation in a range of good precision possible. While the digital titrator is more expensive than other test kits the fact that cartridges are available for other tests such as hardness and chloride tend to make the cost some what less burdensome .

Figure 2.2   Digital Titrator. Shown here mounted to stand via mounting fixture which can also accomodate pH electrode, RTD. Can also be operated hand held in which case a straight dip tube is used

Another interesting approach to simplification of water testing procedures is used in the Titrets® offered by Chemetrics of Calverton, VA (Cat. K-9819 0 - 100 mg/L). These are illustrated at the right of Figure 2.3. A Titret is an evacuated ampoul which contains a premeasured amount of hydrochloric acid. A small sample of the water to be tested in placed in a sample cup and an indicator (bromcresol-gree/methyl-red) is added. The ampoule is fitted with a small diameter plactic tube containing a ball valve and the assembly placed in a plastic holder which features a lever that, when depressed, squeezes and opens the ball valve. The drawn glass tip of the ampoule is broken off within the plastic tube and the free end of the plastic tube placed below the surface of the water. The lever is operated carefully which results in the vacuum within the ampoul drawing water up into it. Water is admitted in small portions until the indicator changes color in the reverse direction i.e. with small quantities of water admitted the acid will predominate and the indicator will be the pink color of this indicator at low pH. As more water is admitted the acid is neutralized by the bicarbonate in the sample to the point where the pH increases enough that the indicator turns green, the color it is in the sample jar. At this time the ampoule is inverted and the amount of alkalinity read from graduations printed on the side of the ampoule. The more water required to "neutralize" the acid in the ampoule, the lower the alkalinity. This process is called "reverse titration" both because it is the sample which is admitted in controlled amounts rather than the acid and because the color change is in a direction the reverse of usual.

Alkalinity can also be measured with kits obtained from an aquarium supply store. An aquarium supply store is often, as was the case with the chlorine kits mentioned in Ref. 1., the easiest and quickest place to obtain a test kit. The kit made by Red Sea Fish pHarm Ltd. (Figure 2.3, left) does both pH and alkalinity tests and is a great favorite of mine because it reads in mEq/L instead of ppm as $CaCO_3$. The range of the kit is 0 to 3.6 mEq/L (0 - 180 ppm). Ten mL of water are placed in a test tube and an indicator added. The color of the water is compared to that of patches (7 span the range) printed on the side of the carton and on a separate card.

Figure 2.3   **Alkalinity Test Kits. Left to right: Aquarium, Drop Titration, Reverse Titration Evacuated Ampoul**

3.0　　　　Hardness

3.1　　　　Definition of Hardness

The term "hardness" refers to the concentrations of calcium and magnesium, and only these two elements, in a water sample. This leads to some confusion because one can argue, and some do, that other elements such as strontium which is found at fairly high concentration in some wells should be included because it behaves very similarly to calcium and magnesium and will be measured by most simple tests. Nevertheless, the definition of hardness, and again the authority is Ref. 6., excludes all but calcium and magnesium.

Calcium is a soft white metal with a molecular weight of 40 and an equivalent weight of 20 (it forms a doubly charged cation). Magnesium is a harder, silvery, light, less reactive metal with a molecular weight 24.30. It also forms doubly charged cations and thus has an equivalent weight of 12.15. Concentration of the ions can be expressed either in terms of the weight of the metal per liter of sample (mg/L or ppm), in terms of the normality (mEq/L) or in ppm as $CaCO_3$. Measurements in mg/L are converted to mM/L by dividing by the molecular weight and to mEq/L by dividing by the equivalent weight. mEq/L are converted to "as $CaCO_3$" by multiplying the mEq/L by 50 or to mg/L by multiplying by the equivalent weight. Also, "as $CaCO_3$" are converted to mEq/L by dividing by 50.

Hardness is often subdivided into calcium hardness and magnesium hardness. It can also be subdivided into permanent and temporary hardness. Calcium hardness is the part of the hardness caused by calcium ions in the sample. It is the calcium ion concentration expressed either in mEq/L or ppm as $CaCO_3$. Magnesium hardness is the magnesium ion concentration in the sample expressed either in mEq/L or ppm as $CaCO_3$. Total hardness is the sum of the calcium and magnesium hardnesses. Thus hardness is reported in the same units as alkalinity and this is convenient both in terms of calculations involving hardness and alkalinity, which we will get into in Part II, and in measurement of hardness which is done the same way as alkalinity but with different titrants and indicators. As an example consider a water sample containing 30 mg/L calcium and 36.45 mg/L magnesium. The calcium hardness is 30/20 = 1.5 mEq/L. Fifty times this gives 75 ppm as $CaCO_3$. The magnesium hardness is 36.45/12.15 = 3 mEq/L or 150 ppm as $CaCO_3$. The total hardness is 4.5 mEq/L or 225 ppm as $CaCO_3$. Note that in this example two thirds of the hardness comes from the magnesium even though its concentration by weight is a little over half that of the calcium.

Temporary hardness is that hardness which could theoretically be removed by precipitation of all the calcium and magnesium as their carbonates. Thus it is the amount of hardness for which bicarbonate is available, on a mEq/L basis, if carbonate is the limiting species and the amount of carbonate for which calcium and magnesium are available if these are limiting. Thus if the total hardness is greater than the alkalinity, the temporary hardness is the alkalinity. Subtract the alkalinity from the total hardness to obtain the permanent hardness which is just the hardness that is not temporary. If the alkalinity is greater than the total hardness, the total hardness is the temporary hardness i.e. all the hardness is temporary and there is no permanent hardness. The usual units for temporary and permanent hardness are ppm as $CaCO_3$ though mEq/L can certainly be used.

3.2　　　　Measuring Hardness

Most readers are aware that hard water results in the formation of curds (calcium/magnesium stearate) when soap (sodium stearate) is added it. The original method of hardness measurement involved adding special soap solution to a water sample until all the calcium and magnesium had precipitated after which additional soap would result in the formation of suds. The details of this method can be found in Ref 8. Hach Company sells a soap based kit (Model SO-1; total hardness only) which is more for demonstration of increased soap consumption in hard water than accurate measurement but it is suprisingly accurate nevertheless.

Hardness is most precisely measured using Atomic Absorbtion Spectromety (AAS). Brewers are unlikely to encounter this method of measurement though samples sent to large laboratories may well be analyzed using this technique. AAS (see Ref. 6.) measures the amount of light absorbed by ionized atoms of the metal in the sample and is more (though not totally) immune to interferences from other substances in the sample than the more conventional chemical tests.

The home or craft brewer is most likely to use a kit similar to an alkalinity test kit to measure hardness. In most an indicator which forms a highly colored (usually deep red) complex with the metals is added to sample. A chelating agent (i.e. a substance that binds the metal closely) of calibrated strength is then titrated into the sample. The end point of the titration is reached when all the metal ions which participated in forming the color complex with the indicator are bound to the chelating agent. The indicator changes color at the end point, usually to a bright blue. The number of mEq of chelating agent required to effect this color change is equal to the number of mEq of the metal in the sample. In some specialized (high sensitivity) tests a fixed amount of chelant and indicator is added to the sample and the color change measured with a spectrophotometer.

The simplest tests measure only the total hardness. A buffer is added to the sample to raise the pH to the point (usually about pH 10) where the indicator works best, the indicator is added and then the chelant is titrated until the color change occurs. Sample size and titrant strength are adjusted so that calculation is simplified. For example in a kit made by Aquarium Pharmaceuticals (Product No. 48A; total hardness only) titrant is dispensed from a dropper bottle and each drop of titrant corresponds to 10 ppm as $CaCO_3$.

Where separate values for calcium and magnesium hardness are required one is measured and subtracted from the total to give the other. A common scheme (example Hach Model HA-4P Catalogue 1457-01) first tests total hardness with a proprietary indicator and pH 10.1 buffer. The titrant (dispensed by eyedropper in this kit) is EDTA (ethylene diamine tetraacetic acid, the most common chelating agent). After total hardness is determined a separate test in run in which the pH is raised (with potassium hydroxide) to the point where magnesium hydroxide precipitates thus in effect removing it from the solution. (In Part II I'll show how this same trick can be used to remove excess magnesium from water.) The indicator (not the same one used for the total test) then reacts only with the calcium and the amount of EDTA required to bring about a color change is proportional only to the calcium hardness. Other schemes use indicators which respond to only calcium or magnesium or chelating agents which selectively bind to one or the other.

Hardness can be measured by reverse titration and Chemetrics makes Titrets® ampoules for total and calcium hardness. EDTA (ethylene diamine tetraacetic acid, the most common chelating agent) cartridges are available for the Hach digital titrator and bottled solutions of EDTA of calibrated strength can be obtained for use with conventional burets. Recently test strips (example Hach Cat 27452-50; total hardness only) have come on the market.

4.0 Significance of Alkalinity and Hardness in Brewing - Preview of Part II

Now that you know what alkalinity and hardness are and how they are measured it is reasonable to ask what influences they have on beer. This will be the subject of Part II of this series. For now we will offer just the generalization that alkalinity is usually thought of as bad and hardness as good. High alkalinity tends to keep mash pH higher than desired. Alkalinity is caused by carbonate and bicarbonate and as such is thought to have a negative effect on beer flavor even when these ions are neutralized. Alkalinity under 50 ppm as $CaCO_3$ is generally considered desirable though many beers are brewed with water more alkaline than that.

While alkalinity is generally considered a problem calcium (hardness) is usually thought of as beneficial by brewers. It lowers mash pH by reaction with malt phosphate, protects alpha amylase from heat, stimulates mash enzymes facilitates break formation and improves yeast flocculation. Some should survive all the way through to the beer in order to facilitate the precipitation of oxalate. Fifty to 100 mg/L in the mash is often given as a desireable level though, again, many beers are brewed with waters much softer (and harder) than the 125 - 250 ppm as $CaCO_3$ calcium hardness implied by this level. Many brewers add calcium chloride or calcium sulfate to their mashes or brew water both to lower pH and to acheive the flavor modifications that sulfate and chloride ions provide.

Magnesium has the pH lowering properties of calcium but to a lesser extent. Each mEq/L of magesium hardness has about half the pH lowering effect of a mEq/L of calcium hardness. Magnesium is also a yeast enzyme cofactor and increases the resistance of yeast to the stresses of temperature change and high alcohol concentration [Ref. 10.]. Magnesium in excess, however, lends a sour bitterness to beer and is, especially when paired with sulfate, laxative. It is generally considered desireable to keep magnesium levels below 30 mg/L though there are beers brewed with water which contains much more than this.

As magnesium and calcium lower pH and alkalinity raises it it seems reasonable that we might be able to predict mash pH by comparing their values. This is indeed so and the usual comparison measure is called Kohlbach's Residual Alkalinity. Not only does RA allow the brewer to estimate what happens when his water hits his grist but it serves as a useful way of grouping and classifying water samples. I will be discussing Kohlbach's RA and its relationship to mash pH in detail in Part II of this article. The rest of Part II is dedicated to discussions of means for reducing and increaing alkalinity and hardness in brewing water.

5.0 Alkalinity Calculations (Sidebar)

In this sidebar I'll give a few of the formulas necessary to work with alkalinity quantitatively. I won't give detailed derivations - just enough so that anyone interested can work out the details. These formulas are somewhat simplified but are plenty accurate for most brewing work. You may contact me at ajdel@mindspring.com if you have questions or want fuller details.

5.1 Basics

Key in the quantitative understanding of carbonate chemistry are the two ratios

$$r_1 = 10^{pH - pK_1} \tag{5.1}$$

and

$$r_2 = 10^{pH - pK_2} \tag{5.2}$$

where pK_1 and pK_2 are constants which depend on temperature and have nominal values, at 25°C of, respectively, 6.48 and 10.33 (see Ref. 2.). r_1 is the molar concentration of bicarbonate ions in the sample divided by the molar concentration of carbonic. r_2 is the molar concentration of carbonate divided by the molar concentration of bicarbonate. Thus if there are x moles of carbonic in a sample at a particulare pH, there are xr_1 moles of bicarbonate and

xr_1r_2 of carbonate. The total number of carbo moles is then

$$C_T = x(1 + r_1 + r_1r_2) \tag{5.3}$$

and the fraction which is carbonic is

$$f_1 = \frac{x}{C_T} = \frac{1}{1 + r_1 + r_1r_2} \tag{5.4}$$

It's handy to define $d = 1 + r_1 + r_1r_2$ then

$$f_1 = 1/d \tag{5.5}$$

The fraction of carbo which is bicarbonate is simply r_1 times the fraction which is carbonic

$$f_2 = r_1f_1 = r_1/d \tag{5.6}$$

and the fraction which is carbonate is r_2 times the fraction which is bicarbonate

$$f_3 = r_2f_2 = r_1r_2/d \tag{5.7}$$

Figure 2.1 is constructed by evaluating Equations (5.5), (5.6) and (5.7) for several values of pH and plotting. You can do this with any visualization or spreadsheet program with plotting capability. If you fully understand Figure 2.1 you have mastered 90% of brewing water chemistry.

Earlier in this article(Section 2.4) I indicated that alkalinity, in mEq/Ls, is twice the number of moles of carbonate plus the number of moles of bicarbonate:

$$Alk_{mval} = [HCO_3^-] + 2[CO_3^{-2}] \tag{5.8}$$

Brackets surrounding a chemical symbol indicate the molar concentration of that species. I just showed that the molar concentration of carbonate is r_2 times that of bicarbonate so

$$Alk_{mval} = [HCO_3^-] + 2r_2[HCO_3^-] = (1 + 2r_2)[HCO_3^-] \tag{5.9}$$

and

$$[HCO_3^-] = \frac{Alk_{mval}}{(1 + 2r_2)} \tag{5.10}$$

are the relationships between alkalinity and bicarbonate content when the alkalinity is in mEq/L and the bicarbonate in mM/L. The carbonate molarity is simply obtained from the bicarbonate from

$$[CO_3^{-2}] = r_2[HCO_3^-] \tag{5.11}$$

Similarly, the carbonic can be calculated from

$$[H_2CO_3] = [HCO_3^-]/r_1 \tag{5.12}$$

5.2   Calculating Carbo Species Concentrations from Alkalinity (Sidebar)

The equations in the last section can be used to calculate the concentrations of individual carbo species from alkalin-

ity. Alkalinity is usually expressed in ppm as $CaCO_3$ while carbonic, bicarbonate and carbonate are in mg/L. Thus conversions must be done. The following steps show you how to compute bicarbonate and carbonate from alkalinity. As an example let us suppose that we have water with alkalinity of 80 ppm as CaCO3 at pH 8.0. Values calculated for this example follow each step in brackets. Many more decimal places than are really necessary are given so you can compare your calculations to mine.

1. Calculate r_1. [33.11311]

2. Calculate r_2. [0.004677]

3. Convert alkalinity expressed in units of ppm as $CaCO_3$ to alkalinity in mEq/L, if necessary, by dividing by 50. [1.6]

4. Compute the concentration of bicarbonate in millimoles per liter by Eqn (5.10). [1.585172]

5. Convert bicarbonate concentration in mM/L from Equation (5.10) per liter to mg/L by multiplying by 61, the molecular weight of bicarbonate ion. [96.7]

6. Compute the concentration of carbonate in millimoles per liter using Equation (5.11). [0.0074138]

7. Convert carbonate concentration in millimoles per liter to mg/L by multiplying by 60, the molecular weight of carbonate ions: [0.4448]

8. Calculate the carbonic concentration using Equation (5.12).[0.04787]

9. Convert the carbonic concetration to mg/L by multiplying by 62, the molecular weight of carbonic acid [2.97 mg/L] or to "as CO_2" by multiplying by 44, the molecular weight of CO_2. [2.11 mg/L]

You will find in most cases (pH < 8.3 or so) that r_2 is much smaller than r_1. In these cases the bicarbonate ion concentration in mg/L can be approximated simply by dividing alkalinity in ppm as $CaCO_3$ by 50 and then multiplying by 61. The carbonate ion concentration is very small in these cases but can be easily approximately calculated by multiplying the bicarbonate concentration by r_2 and then multiplying by 60.

5.3   Estimating Alkalinity from Carbonate or Bicarbonate Ion Concentration (Sidebar)

The formulas of Section 5.1 can also be used to calculate the alkalinity from the concentration of any of the three carbo species. It is not common, but occasionally one may find bicarbonate listed on a water report rather than the alkalinity. Unfortunately, when this is done, the value is frequently labeled as "carbonate" when bicarbonate is really meant. This is particularly likely in listings of water properties in books and articles. As Figure 2.1 shows there is, in fact, very little carbonate is any water with pH less than about 9.

To estimate the alkalinity from one of the carbo species, do the following steps. Assume, as an example, that the pH is 7 and that you know one of the following: bicarbonate concentration is 122 mg/L, carbonic concentration is 34.15 mg/L as carbonic acid or carbonate ion concentration is 0.05613 mg/L. The numbers in brackets following each step are the values calculated for this example.

1. Calculate r_1 [3.6307] and r_2 [0.00046773]

2.   If starting from carbonic convert to mM/L by dividing the mg/L value "as CO2" by 44 or the mg/L value as carbonic acid by 62 [0.5508]. Then multiply by r_1 to get mM/L bicarbonate [1.9998].

3.   If starting from carbonate (being first really sure that carbonate is meant) mg/L, divide by 61 to convert to mM/L [0.000935]. Then divide by r_2 to get mM/L bicarbonate. [2.00008]

4.   If starting from bicarbonate divide the bicarbonate ion concentration by 61 [2.0000]

5.   Use Equation (5.10) to calculate the alkalinity i.e. multiply the mM/L bicarbonate by $1 + 2r_2$ to get the alkalinity in mEq/L (mEq/L). [2.00187]

6.   Multiply the alkalinity in mEq/L by 50 to get the value in ppm as $CaCO_3$. [100.09]

5.4   Increase in Alkalinity From Added Carbonate or Bicarbonate

Another related calculation determines the amount of increase in alkalinity caused by the addition of a measured amount of calcium carbonate (chalk) or sodium bicarbonate (baking soda). As an example assume that 42 mg/L sodium bicarbonate or 25 mg of calcium carbonate is to be addded to each liter of water. :

1.   If using sodium bicarbonate convert the mg/L to mEq/L by dividing by 84, the equivalent weight of sodium bicarbonate. [0.5] This is the increase in alkalinity in mEq/L.

2.   If using calcium carbonate, covert the mg/L to mM/L by dividing by 50, the equivalent weight of calcium carbonate.[0.5] This is the increase in alkalinity in mEq/L.

3.   Multiply by 50 to get the increase in alkalinity in ppm as $CaCO_3$. [25]

Note that calcium carbonate in any quantity will not dissolve in water so that it is usually added to the mash rather than the water. I'll have more to say about this in Part II.

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