Water Quality

"Pure" water? NOT!

There is no such thing as "pure" water. Water is known as the "universal solvent" because it readily dissolves things into it. Whether water is at the surface of the earth or underground, it is in contact with soil or rock and will dissolve it to some extent. Water that is in the atmosphere will dissolve gases into it (e.g. rainwater dissolves carbon dioxide making it slightly acidic naturally, or it may dissolve sulfur that is present in high concentrations due to industry and create even more acidic rain.) Therefore, it is basically impossible for water to be simply composed of just hydrogen and oxygen.

However, we can get close to having "pure" water by distilling it. Distillation is the process of heating a mixture and condensing the resulting vapor to produce a more nearly pure substance. It is one of the basic principles used in the desalinization of seawater and is in fact used by US Navy vessels to supply drinking water on-board. While distillation can be costly in terms of energy and money, the cost is slowly decreasing and it is becoming more commonplace to see tabletop water distillers available for home use, just as water filtration systems are being used now.

The natural evaporation of seawater is a distillation process: the sun heats water, causing it to evaporate, leaving most of the salts behind. As water vapor cools in the atmosphere, it condenses and forms clouds, which then leads to precipitation. As water precipitates back to earth, it can pick up atmospheric particulates and gases.

A functional definition of "salt"

In terms of water quality, a functional definition of a "salt" would be an inorganic, ionic compound that dissolves readily in water to form ions. When water flows over rocks or soil, it dissolves some of the solid minerals it comes in contact with. For example, if water flows over limestone (calcium carbonate) it dissolves the rock to form calcium (Ca^{+2}) ions and carbonate ions (CO_3^{-2}) in the water. Likewise, when water is in contact with solid sodium chloride ($NaCl$), it is dissolved into (Na^{+1}) and (Cl^{-1}) ions. When water is evaporated from water containing salt ions, it forms solid salt again.

Remember as a child, going to the beach and rinsing off your sand shovel and bucket in the ocean? Later the rinse water has evaporated, leaving a crust on your tools. This crust is a combination of many different salts besides sodium chloride ($NaCl$). While the crust will mostly be sodium chloride (since 78% of the salt in seawater is $NaCl$), the crust may also contain potassium chloride, magnesium chloride, magnesium sulfate, calcium sulfate, and calcium carbonate. The total salts (crust) that form when water is evaporated are "dissolved solids."

How to estimate how "salty" water is

There are three common ways to measure how "salty" water is. One is to measure salinity which measures only the amount of sodium chloride in water. We won't be dealing with salinity in this class. The other ways are to measure Total Dissolved Solids (TDS) or electrical conductance.

Total Dissolved Solids (TDS)

In the laboratory, we can determine the concentration of dissolved solids in the water by evaporating a filtered sample of a known volume and weighing the resulting solids that form. The weight of the dissolved solids divided by the volume of water used is a measurement called "Total Dissolved Solids" or TDS. This is a very easy procedure to do but it is very time consuming.

- determined by evaporating a known volume of water and measuring the evaporated salt
- measures the total concentration of dissolved salts in water
- doesn't tell you what type of salts are present

Specific Conductance (Electrical conductance)

If you are in the field and you want a quick method for estimating the dissolved solids concentration, you can test the specific conductance of water. This is done by dipping a set of electrodes into the water and measuring, usually on a digital meter, the amount of electrical current flowing between the electrodes. In order for electrical current to flow through water (and from one electrode to the other for current to be measured) there must be ions present. As the ions are attracted to the electrodes, they produce electrical current which is measured. The more ions, the more current produced. And of course, the more ions in solution, the more dissolved salts in the water.

However, there may be some ions in water that produce electrical current but would not form salts if the water was evaporated. For example, if hydrochloric acid (HCl) was dissolved in water, it would form H^+ and Cl^- ions in water. Those ions would cause electrical conductance of water, but would not form a solid salt if water was evaporated. Therefore, you can see how specific conductance is usually higher than the Total Dissolved Solids concentration. TDS (in mg/L) is typically half to two-thirds of the specific conductance value (in microSiemens/cm).

- Measured by dipping two electrodes into water to determine the ability of the solution to carry an electrical current
- varies with the total quantity of dissolved ions (charged particles), whether they are salt forming ions or not
- does not tell you what type of ions are present

Other Water Quality Parameters Involving Ions in Water

Hardness

Water that is hard does not lather well when soap is added, may form hard deposits on hot water heaters, and may taste funny. Water is hard if it contains a lot of ions that have a (+2) charge. Primarily, water is "hard" because of the presence of calcium (Ca^{+2}) and magnesium (Mg^{+2}) , which are the most common (+2) ions dissolved from rock material that water has been in contact with. These ions like to combine with soap before it has a chance to attack dirt, rendering it useless. Also, as hard water increases in temperature, the (+2) ions like to attach to other ions in water to form a hard precipitate or scale or water pipes (e.g. calcium carbonate.)

- measured as the concentration of calcium and magnesium ions in water

pH

pH is a way of expressing how acidic or basic a solution is. pH is defined as the negative logarithm of the concentration of hydrogen ions in solution. pH is a number and does not have units. pH ranges from 1-14, where a pH of 7 is neutral, pH of less than 7 indicates that water is acidic, and pH greater than 7 indicates that water is basic or alkaline.

When water is "pure", hydrogen ions (H^+) and hydroxyl ions (OH^{-1}) are continually bonding and breaking bonds (because water is a liquid), and these two ions are present in equal amounts. However, when acids are added to water (for example, HCl), they dissolve (to form H^+ and Cl^- ions) upsetting this balance. There are now more H^+ ions than OH^{-1} in solution so the water becomes acidic and decreases in pH. If there is carbonate (CO_3^{-2}) also in this water, then some of the H^+ ions might combined with CO_3^{-2} to form HCO_3^-, taking some H^+ ions out of solution. Thus, the solution would become more basic and the pH may rise. pH reflects the concentration of H^+ ions floating around in solution (not combined to anything.)

Since pH varies logarithmically, we can see that a solution with a pH of 4 is 10 times as acidic as a solution with a pH of 5 and 100 times as acidic as a solution with a pH of 6.

- can be measured using indicator solution or indicator paper (litmus, etc) or can be measured using an electrode
- is a measure of the concentration of hydrogen ions (H^+) in solution
- measures the relative strength (how acidic of alkaline) of the water in terms of the amount of hydrogen ions present, but it does not reflect the ability of that solution to resist changes in pH.

Alkalinity

Alkalinity is the buffering capacity of water, or the ability of water to resist changes in pH. It is possible to have two different waters that have the same pH but different alkalinities. Water that has a lot of carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), or hydroxide (OH^{-1}) will have high alkalinity because you will be able to add amounts of acid to the water without having the water change in pH. This is because carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), and hydroxide (OH^{-1}) like to combine with the hydrogen ions added by the acid. When these alkalinity ions combine with H^+ added by the acid, it takes H^+ out of solution and therefore keeps it from impacting the pH. If water doesn't have much carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), and hydroxide (OH^{-1}), H^+ added to the solution would have nothing to combine with and would stay in solutions, thus decreasing the pH.

- measures the concentration of carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), and hydroxide (OH^{-1}) in solution
- reflects the ability of water to resist changes in pH

pH, Alkalinity, and Hardness

pH and Alkalinity

Background:

Many compounds, including water, are capable of disassociating, or ionizing, to form positively and negatively charged ions. In the case of water, this dissociation results in the formation of two ions in the solution: a positively charged hydrogen ion (H^+) and a negatively charged hydroxide ion (OH^-). The hydrogen ion is sometimes referred to simply as a "proton" because it carries the single positive charge of a proton.

A compound that is capable of dissociating into a hydrogen ion and an "anion" (negatively charged ion) is said to have acid character. For example, hydrochloric acid (HCl) dissociates into H^+ and Cl^- ions and is an acid because H^+ ions are formed. Table salt (NaCl), however, dissolves into Na^+ and Cl^- ions and does not form H^+ ions. Therefore, NaCl is not an acid. The more easily an acid dissociates, the more acidic it is.

Since water is the most abundant solvent on the earth's surface, pure water is taken as the standard by which other compounds with acid character are classified. Pure water itself dissociates by a process called **self-ionization**. This process is a reaction in which two like molecules (two water molecules) react to gives ions. In the case of water, this is an ongoing process.

$$H_2O\ (l)\ \_\_\ H^+\ (aq) + OH^-\ (aq) \qquad (1)$$

Where H_2O (l) = liquid water
H^+ (aq) = "aqueous" hydrogen ion
(hydrogen ion in solution)
OH^- (aq) = aqueous hydroxide ion

The forward and reverse arrows show that this reaction proceeds in both directions. That is, water molecules dissociate to form ions while at the same time other hydrogen ions and hydroxide ions recombine to form water molecules again.

In pure water, a dynamic equilibrium between the forward and reverse reaction is obtained when the concentration of the hydrogen ions [H^+] is equal to 10^{-7} moles per liter (written 10^{-7} M). A "mole" of anything is equal to the quantity 6.022×10^{23} of it, just like a dozen of

anything is equal to 12 of it. Therefore,

$$10^{-7} \text{ moles/liter} = 10^{-7} \text{ moles/liter} \times (6.022 \times 10^{23} \text{ ions/mole})$$
$$= 6.022 \times 10^{16} \text{ ions/liter.}$$

Since a water molecule must form a hydroxide anion for every hydrogen ion, the concentration of hydroxide ions in pure water is exactly the same as the concentration of hydrogen ions (written [H^+]). Therefore, the concentration of OH^- ([OH^-]) equals 10^{-7} M.

6.022 x 10^{23} hydrogen ions per liter looks like a large number. But it is not very large compared to the number of water molecules in a liter of water (3.35 x 10^{25}).

Acids and Bases:

We are all familiar with acids and bases. Lemon juice, which makes our lips pucker, is an acid. Antacids are designed to "neutralize stomach acid" so antacids themselves are bases. What is more acidic, battery acid or lemon juice? Off hand we would say battery acid is more acidic because we know it would be bad to ingest it. If two substances are both acidic, what determines if one substance is relatively more acidic than the other?

We mentioned earlier that pure water self-ionizes to form hydrogen ions (H^+) and hydroxide (OH^-) ions. When there is an equal amount of H^+ and OH^- ions in a solution, the solution is in dynamic equilibrium and is said to be neutral. If we add an acid to the water, the acid will also dissociate, donating H^+ to the solution. If the acid is a strong acid, the amount of H^+ dissociated with the self-ionization of water molecules is negligible compared to the amount of H^+ donated by the strong acid. Since the only source of OH^- in the solution is from self-ionizing water molecules, and the since the H^+ and OH^- donated by self-ionization is negligible compared to the amount of H^+ donated by the strong acid, there is much more H^+ in solution than OH^-. Therefore, the solution is acidic because there are more H^+ ions in the solution than there are OH^- ions.

Addition of hydrogen ions (H^+) adds acidity to a solution. Addition of hydroxide ions (OH^-) makes a solution more basic.

If [H^+] > [OH^-], then the solution is acidic.
If [H^+] = [OH^-], then the solution is neutral.
If [H^+] < [OH^-], then the solution is basic.
* Brackets mean concentration.

To answer the question above, the degree of acidity depends on the concentration of hydrogen ions in the solution. If there are two acidic solutions, the lemon juice and battery acid for example, the one which contains more hydrogen ion would be the more acidic one.

pH:

pH is a way of expressing how acidic or basic a solution is. Since the degree to which a solution is an acid or base depends on the amount of H^+ in the solution, the pH is a way of describing the concentration of hydrogen ions.

$pH = -\log [H^+]$ (2)

Conversely,

$[H^+] = \text{antilog} [-pH]$ (3)

The pH of a solution is a unitless number.

For example, if you have a solution and someone was able to measure the H^+ concentration, and found,

$[H^+] = 10^{-8.5}$ M

* M means Molarity (moles per Liter). This is a concentration unit.

then using Equation (2), we find would solve for the pH as follows:

$$\begin{aligned} pH &= -\log[H^+] \\ &= -\log[10^{-8.5}] \\ &= 8.5 \end{aligned}$$

It is easy to find the pH of a solution when its hydrogen ion concentration is in the form of 10^n because the pH is simply the negative of the exponent. Using this trick, we obtain the same answer as when we used Equation (2).

$$\begin{aligned} [H^+] &= 10^{-8.5} \\ pH &= -(-8.5) \\ &= 8.5 \end{aligned}$$

But if the concentration is a **number times 10^n**, then Equation (2) must be used. For example, to find the pH of a solution with $[H^+] = 5 \times 10^{-6}$, use Equation (2) as follows:

$$\begin{aligned} pH &= -\log[H^+] \\ &= -\log[5 \times 10^{-6}] \\ &= 5.30 \end{aligned}$$

If you are given a pH and you need to find the concentration of hydrogen ions, use Equation (3).

Recall that a logarithm is the exponent of a number written to the base ten. The negative logarithm ("log") would be the negative exponent. Therefore, a seemingly small increase in pH is actually a much larger increase in H^+ or acidity of the solution. For example, a one unit increase in pH results in a solution which is 10 times less acidic.

For	pH $= 4.0$	pH $= 5.0$
	$[H^+]$ = antilog $[-4.0]$	$[H^+]$ = antilog $[-5.0]$
	$= .0001$	$= .0001$
	$= 10^{-4}$ M	$= 10^{-5}$ M

The solution with a pH of 5.0 has 10 times less H^+ ions than the solution with a pH of 4.0 and is therefore 10 times less acidic than the pH 4.0 solution.

Why is pH used to describe how acidic a solution is? Why don't we just talk in terms of hydrogen ion concentrations?

Hydrogen ion concentrations are generally very small (ex. 10^{-8}) and it is not very convenient to write these numbers out. Plus, as will be discussed later, pH is easily measured with scientific instruments. Therefore, pH is commonly used as a shorthand method of writing these numbers.

The pH scale has a range of 0-14. In very rare instances, the pH of a solution can be negative or greater than 14, however, it is not easily measurable. The pH scale of 0-14 is sufficient to cover the solutions we see in the experience of everyday life.

pH < 7 Acidic $[H^+] > [OH^-]$
pH $= 7$ Neutral $[H^+] = [OH^-]$
pH > 7 Basic (alkaline) $[H^+] < [OH^-]$

Pure water has a pH of 7. But if something is added to the water that itself dissociates (dissolves) to form hydrogen ions and anions, the hydrogen ion concentration will increase. Such substances are called acids. One common acid that dissolves to form hydrogen ions and chloride ions is hydrochloric acid (HCl). The equation for the chemical reaction is written:

$$HCl \longrightarrow H^+ (aq) + Cl^- (aq) \qquad (2)$$

Equation (2) has an arrow pointing only to the right. This is because HCl is a "strong" acid. It completely dissociates and the hydrogen and chloride ions do not recombine to form HCl molecules in the solution.

The pH of pure water is the pH of a so-called neutral solution. If the pH is lower than 7 (hydrogen ion concentration greater than 10^{-7}), then the solution is considered to be acidic. If the pH is higher than 7 the solution is basic or alkaline. In most natural waters, the pH is

between about 6 and 9. Rainwater (unpolluted) has a pH value near 5.3. Acid rain may have a pH as low as 1.5. Fish, water plants, and other aquatic life have adapted to certain ranges of pH, and a pH outside this range can have harmful effects.

pH is one of the primary influences on the solubilities of substances in water. Acidic waters can have high concentrations of metal ions, while basic or "alkaline" waters may contain abundant salts. Thus, pH is an important water quality parameter.

Two different methods will be used to measure the pH values of some water samples and household products. The colormetric method is based on the principle that certain substances (indicators) change color in water of different pH values. The observed color can then be compared to a calibration chart to determine the pH.

The potentiometric method for measuring pH measures the potential of an electrode immersed in the water sample. The electrode potential varies with pH in a known manner, such that the instrument translates the potential into a direct reading of pH.

****Before leaving lab be sure you can convert between pH and [H^+], ask your instructor if necessary****

<u>Alkalinity:</u>

pH is a way of measuring the hydrogen ion concentration of a solution. Two solutions that have the same pH may have different alkalinities. The two words "alkaline" and "alkalinity" mean different things. When we measure the pH of a solution, we can say it is either acidic or alkaline based on the amount of hydrogen ion it contains in solution. We cannot, however, tell anything about the alkalinity of the solution if we only determine its pH. This is because **alkalinity** is a measure of the solution's ability to neutralize acids. In other words, alkalinity answers the question " how much acid can we add to this solution before its pH changes significantly? "

A buffer is a solution that can resist changes in pH when limited amounts of acid or base are added to it. Natural water has an ability to resist changes in pH because ions such as **hydroxide (OH^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-)** are dissolved into the water from rock materials. These are the primary ions responsible for giving water this buffering ability. These ions like to combine to free hydrogen ions. When H^+ ions are bound to one of the above ions in the carbonate system, the H^+ ions are no longer in solution and therefore, do not contribute to change the pH of the solution. Alkalinity is a measure of the buffering capacity of a water.

Alkalinity is an important water quality parameter, especially for surface waters such as streams, rivers, and lakes. Acid rain and acid mine drainage (water that becomes acidic after it flows over mine spoils) can decrease the pH of water bodies if the water does not have a high enough alkalinity. As mentioned above, certain fish and aquatic species require certain pHs to live and if the pH becomes depressed suddenly by a acid water from a rain storm, fish kills can result.

Hardness:

Background:

Hardness is a way to measure specific ions in the water that cause "hardness". Hardness refers to the concentration of certain "divalent" (meaning with a charge of +2) cations (cations are positively charged particles), mainly calcium (Ca^{+2}), and magnesium (Mg^{2+}) in the water. Other divalent cations contribute to hardness. Strontium (Sr^{2+}), iron (Fe^{2+}), and manganese (Mn^{2+}) are examples. But calcium and magnesium are the most important since they are the most abundant in most waters. The source of the cations is usually the rock through which the water has flowed. Calcium ions are dissolved from rock such as limestone or dolomite, or from sandstone that contains calcite ($CaCO_3$) cement. Limestone is primarily made of the mineral calcite. Dolomite is very similar to limestone, except that it has a significant amount of magnesium in its crystal structure. Since these rocks are very common, hard water is also relatively common. Regions containing a lot of limestone often have many caves from where groundwater has dissolved the limestone. Such regions are referred to as karst terrain.

There are two major undesirable characteristics of hard water. One is that it makes soap ineffective. The other is that hard water causes "scale" to form on the inside surface of pipes and boilers, reducing their ability to conduct heat and eventually clogging the pipes.

Tucson water contains a noticeable concentration of hardness. The hard crusty deposit that forms around dripping pipe joints is calcite that precipitates from the water as it evaporates. The gray soapy coating that clings to bathtubs is largely caused by hard water. And stalactites and stalagmites in limestone caves are the result of dissolved calcite being transported and redeposited by the water dripping into the caves.

The reason that hardness makes soap ineffective is that the cations in the water combine chemically with soap molecules and cause the soap molecules to change their characteristics. Instead of remaining dissolved in the water, the soap molecules precipitate and cling to surfaces like bath tubs. When the cations causing hardness are used up by precipitating soap, the soap can again become effective in dissolving grease.

In boilers or hot water pipes, scale forms because the calcite that is dissolved in the water becomes less soluble at higher temperatures. If it dissolved in cold ground water, then heating the water causes the calcite to come out of solution, and it precipitates on the surface of its container.

Water with a hardness of 60 mg/L of $CaCO_3$ is not suitable for some industrial applications. The U.S. Geological Survey categorizes hardness according to the following scale:

HARDNESS SCALE

mg/L $CaCO_3$	
0 - 60	soft
61 - 120	moderately hard
121 - 180	hard
>180	very hard

The concentration that can be tolerated by industries varies with the industry. Hard water can be treated to remove the cations that cause hardness, but the expense of treating the water may prevent an industry from locating in an area with hard water.

One simple qualitative test of hardness is to add soap to the water to precipitate the divalent cations. Quantitative method involves a chemical that combines very strongly with any divalent cations in the water, called EDTA. An indicator can be added to the solution that will change color as soon as there is uncombined EDTA in the water. Thus, by measuring how much EDTA is added until the indicator changes color, one can determine how much divalent cation must have combined with the EDTA. This is the basis of the hardness titration you will perform in the lab.

Hardness is usually measured as though it was all due to calcium carbonate ($CaCO_3$ chemical formula for calcite). It is therefore expressed in "equivalent weights": in mg/L or parts per million (ppm) of $CaCO_3$. An equivalent weight is the molecular weight of a compound <u>per charge</u> of its ions. It is a way of accounting for the contributions of ions with different masses that enter into chemical reactions as a result of their charges and not their masses. After all, a kilogram of strontium ions will not combine with as many soap molecules as a kilogram of calcium ions, since the molecular weight of strontium is less than that of calcium.

If there is a significant contribution to hardness from cations other than calcium, then an adjustment must be made in the reported concentration as mg/L of $CaCO_3$. For the purposes of this lab we will simply assume that calcium is the only significant contributor to the hardness. A more detailed discussion of equivalent weight can be found in most introductory chemistry texts.