## Alkalinity

## Introduction

Alkalinity is a measure of the capacity of water or any solution to neutralize or "buffer" acids. This measure of acid-neutralizing capacity is important how "buffered" the water is against sudden changes in pH .

Alkalinity should not be confused with $\mathrm{pH} . \mathrm{pH}$ is a measure of the hydrogen ion $\left(\mathrm{H}^{+}\right)$ concentration, and the pH scale shows the intensity of the acidic or basic character of a solution at a given temperature. The reason alkalinity is sometime confused with pH is because the term alkaline is used to describe pH conditions greater than 7 (basic).

The most important compounds in water that determine alkalinity include the carbonate $\left(\mathrm{CO}_{3}{ }^{2-}\right)$, bicarbonate $\left(\mathrm{HCO}_{3}^{-}\right)$ions and OH . The ability to resist changes in pH by neutralizing acids or bases is called buffering.

Alkalinity is important to aquatic organisms because it protects them against rapid changes in pH . Alkalinity is especially important in areas where acid rain is a problem.

## Sources of Alkalinity

Important Compounds for Alkalinity:

| $\mathrm{OH}^{-}$ | Hydroxide ion (base) |
| :--- | :--- |
| $\mathrm{HCO}_{3}^{-}$ | Bicarbonate ion |
| $\mathrm{CO}_{3}{ }^{2-}$ | Carbonate ion |

One source of alkalinity is calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$, which is dissolved in water flowing through geology that has limestone and/or marble. Limestone is a sedimentary rock formed by the compaction of fossilized coral, shells and bones. Limestone is composed of the minerals calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$ and/or dolomite $\left(\mathrm{CaMg}\left(\mathrm{CO}_{3}\right)_{2}\right)$, along with small amounts of other minerals. Limestone is converted to marble from the heat and pressure of metamorphic events.

Alkalinity can increase the pH (make water more basic), when the alkalinity comes from a mineral source such as calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$. When $\mathrm{CaCO}_{3}$ dissolves in water, the carbonate $\left(\mathrm{CO}_{3}{ }^{2-}\right)$ can react with water to form bicarbonate $\left(\mathrm{HCO}_{3}{ }^{-}\right)$, which produces hydroxide $\left(\mathrm{OH}^{-}\right)$:
$\mathrm{CaCO}_{3}(\mathrm{~s}) \leftrightarrow \mathrm{Ca}^{2+}+\mathrm{CO}_{3}{ }^{2-}$
$\mathrm{CO}_{3}{ }^{2-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{HCO}_{3}{ }^{-}+\mathrm{OH}^{-}$

The hydroxide ion $\left(\mathrm{OH}^{-}\right)$is a strong base. An increase in $\mathrm{OH}^{-}$concentration will cause the pH to increase.
In addition to rocks and soils, the alkalinity of water can be influenced by: salts, plant activity, and wastewater.


Carbon dioxide and water are converted to carbonic acid through the following reaction:
$\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}$ (carbonic acid)
Carbonic acid provides bicarbonate and carbonate for buffering, just like $\mathrm{CaCO}_{3}$ :
$\mathrm{H}_{2} \mathrm{CO}_{3} \leftrightarrow \mathrm{HCO}_{3}{ }^{-}+\mathrm{H}^{+}$
$\mathrm{HCO}_{3}{ }^{-} \leftrightarrow \mathrm{CO}_{3}{ }^{2-}+\mathrm{H}^{+}$
While conversion of carbon dioxide to carbonic acid produces ions capable of buffering pH , it also causes a decrease in pH (increase in $\mathrm{H}^{+}$) that $\mathrm{CaCO}_{3}$ doesn't. Notice in the reaction that as carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ reacts to form carbonate $\left(\mathrm{CO}_{3}{ }^{2-}\right), 2$ hydrogen ions $\left.\mathrm{H}^{+}\right)$are released into the water.

## Phenolphthalein Alkalinity

Phenolphthalein is an indicator that changes from pink to colorless at pH 8.3 when acid is added ( pH decreases). Water that has a $\mathrm{pH}>8.3$ is said to have "phenolphthalein alkalinity," which is alkalinity due primarily to the presence of carbonate or hydroxide ions. Many water samples have little or no phenolphthalein alkalinity, and therefore remain colorless after adding this indicator to the sample water.

## Total Alkalinity

Total alkalinity is the final endpoint for the alkalinity titration. At pH 4.5 , all carbonate and bicarbonate ions have been converted to carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ :
$\mathrm{HCO}_{3}{ }^{-}+\mathrm{H}^{+} \rightarrow \mathrm{H}_{2} \mathrm{CO}_{3}$
This endpoint for the titration can be identified using a Methyl Orange indicator. The indicator changes from yellow to red at pH 4.5 .

## Measurement

Total alkalinity is measured by titrating the water sample with sulfuric acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)$ to a pH endpoint of $\sim 4.5$. Once the water sample reaches a pH of 4.5 , the three main forms of alkalinity (bicarbonate, carbonate, and hydroxide) have been neutralized.
When titrating for total alkalinity, there are 2 "equivalence points," where pH changes rapidly with small additions of acid - these lie near pH 8.3 and 4.5 . These points can be determined by measuring pH as the acid is added, or by choosing indicators that change color at the pH value of the equivalence point.

## Procedures:

(1) Pipette 100 ml of sample, in an Erlenmeyer flask.
(2) Add 3 drops of phenolphthalein indicator solution to the flask
(3) If the sample become pink, titrate with $0.02 \mathrm{~N}_{2} \mathrm{SO}_{4}$ until become colorles. Record the volume of the acid.
(4) Add 3 drops of methyl orange indicator solution to the flask.
(5) If the sample becomes yellow, titrate with $0.02 \mathrm{~N}_{2} \mathrm{SO}_{4}$ until become red. Record the volume of the acid.
(6) Calculate Total Alkalinity as follows:

Total alkalinity as $\mathrm{CaCO}_{3} \mathrm{mg} / \mathrm{L}=\frac{\mathrm{A} \times \mathrm{N} \times 50 \times 1000}{\mathrm{~mL} \text { of sample }}$
$\mathrm{A}=\mathrm{ml} \mathrm{H}_{2} \mathrm{SO}_{4}$ used , $\quad \mathrm{N}=$ Normality of $\mathrm{H}_{2} \mathrm{SO}_{4} 0.02 \mathrm{~N}$.

Lab Equipment and Use Review Sheet

| Glassware | Function | Glassware | Function | Glassware | Function |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Beaker | Running reactions, mixing chemicals, heating chemicals |  | Accurately measuring/ delivering liquids |  | Running reactions, heating chemicals mixing chemicals easier for mixing than beakers |
| Filter Flask | Used in vacuum filtration |  <br> Round Bottom Flask | Running reactions, heating chemicals mixing chemicals easier for mixing than beakers |  <br> Volumetric Flask | Used to mix chemicals to accurately determine concentration. |
|  | Used for filtering and for adding chemicals without spilling | Cylinder | Used for accurately measuring the volume of liquids. | Test Tube | Used for mixing and heating chemicals and running reactionssmaller quantities than beakers and flasks. |
| Watch Glass | Holding Chemicals, covering beakers during heating | Glass Stirring Rod | For stirring chemicals | Sample Vial | For storing small amounts of chemicals |
| Dropper Pipets | For adding small amounts of chemicals usually by drops | Buchner Funnel | Funnel used for vacuum filtration | Evaporating Dish | Used to evaporate liquids |
|  | Graduated Pipet and Volumetric Pipet are used to accurately measure liquids. ALWAYS USE A BULB. <br> Graduated add varying amounts of liquids. <br> Volumetric add the specified mount |  <br> Polywash Bottle | Used to add chemicals or used to add solvents for cleaning of beakers and other glassware. | Ring Stand with Utility Clamp and Iron Ring | $\downarrow$ tility Clamp used to hold objects on a ring stand. <br> Fron ring used to hold objects above a Bunsen burner flame. Ring stand used to hold various objects. |

