

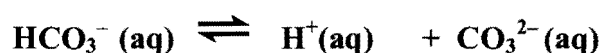
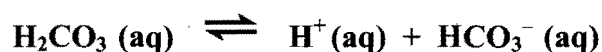
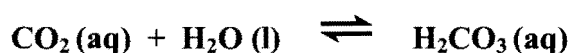
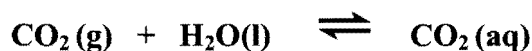
Experiment 4

Alkalinity of Streams and Lakes

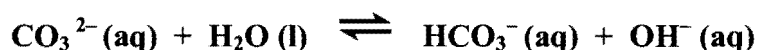
Objective—The objective of this experiment is to introduce a fundamental and very important property of natural waters, the alkalinity. There is a significant difference between alkalinity and basicity, which will be discussed.

Introduction— For several reasons it is important to determine the capacity of a body of water to neutralize acid (hydronium ion). A lake under the influence of acid rain or mine water runoff can absorb only so much acid before its pH begins to drop significantly. The capacity of a water sample to absorb hydronium ion is its alkalinity. Basic water is water that has a pH greater than 7. Alkalinity is a type of buffering capacity and thus a capacity (extensive) factor, whereas basicity is an intensive factor, independent of the quantity of sample.

The pH of many natural waters, as we saw in Experiment 3, is close to 8, and changes in pH are resisted by the presence of a carbonate/carbon dioxide buffer system. Carbon dioxide in water undergoes the following complex equilibria:



Frequently present in the geochemical environment of various water systems are metal carbonates, especially calcium carbonate. In water, calcium carbonate is only slightly soluble due to its small K_{sp} (4.6×10^{-9} at 25°C). However, due to the hydrolysis of carbonate ion,



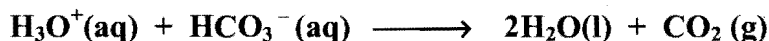
there is an increase in the solubility of calcium carbonate and, therefore, an increase in pH.

If carbon dioxide is also present in the body of water, the following reaction can also occur,



and enhances the solubility of both carbon dioxide and calcium carbonate (Le Châtelier's principle).

When carbon dioxide and calcium carbonate are both present, if a strong acid is introduced into the system, the following reaction occurs,



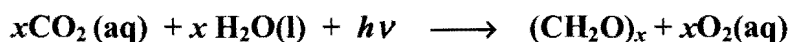
If strong base is added,



Thus, such systems act as buffers where HCO_3^- is the acid and CO_3^{2-} is the conjugate base.

High alkalinity water contains elevated levels of dissolved solids. Although this may be undesirable for boiler water and food processing, it serves as a source of inorganic carbon for the growth of algae and other aquatic life. Hence, alkalinity is a measure of the fertility of the water.

Algae extract the carbon dioxide they need for photosynthesis from aqueous carbon dioxide,



In the absence of sufficient carbon dioxide, bicarbonate dissociates,



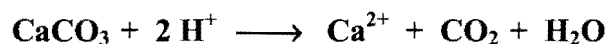
and as algae use bicarbonate, the body of water becomes more basic.

Theory—Alkalinity can be defined as the moles of monoprotic acid per liter needed to react completely with all base present. Since alkalinity is generally due to carbonate, bicarbonate and hydroxide, it is defined by

$$[\text{alkalinity}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}_3\text{O}^+]$$

where the brackets refer to molar concentrations and the coefficients result from the number of H^+ ions the base can react with (for example, CO_3^{2-} reacts with 2H^+). Usually the hydronium ion concentration is small enough to be neglected if the water has a basic pH. In fact, $[\text{OH}^-]$ is usually small compared with the first two terms and can be neglected. There are a few minor contributors to alkalinity, including ammonia and the conjugate bases of phosphoric, boric, silicic, and organic acids.

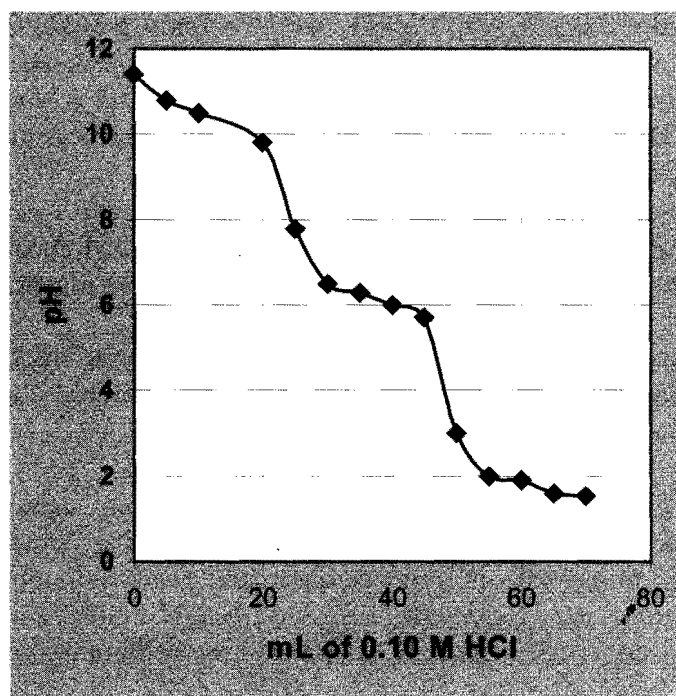
The alkalinity can be expressed in units of mg/L of calcium carbonate, based on the reaction,



If the water is very basic (pH greater than 8.3), a quantity called the phenolphthalein alkalinity can be determined. This is mainly due to the presence of the carbonate ion. In this case the sample is titrated with standard acid to a pH of about 8.3 (where phenolphthalein goes from pink to colorless). Most environmental waters have a pH less than 8.3 and thus have a zero phenolphthalein alkalinity.

When the pH of a sample is less than 8.3, methyl orange is used as the indicator and the water sample is titrated with acid to a pH of 4.3. At this point all the HCO_3^- has been converted to CO_2 . Figure 4-1 shows how the pH varies with titrant volume when a solution of Na_2CO_3 is titrated with acid.

Figure 4-1 Titration of 25 mmol of Sodium Carbonate with HCl



Typical seawater carbonate alkalinity is about 1.2 mmol/L. Anaerobic digesters (used in treating sewage sludge) typically have supernatant alkalinity of 2000–4000 mg/L CaCO_3 .

Safety Issues

1. Safety glasses must be worn at all times in the chemistry laboratory.
2. Avoid skin and eye contact with sodium hydroxide and hydrochloric acid. If contact is made, rinse your

hands or flush your eyes for several minutes.

3. Use concentrated HCl only in the fume hood. Avoid breathing its vapors and avoid skin contact.

Procedure—The sample should not be filtered, diluted, or concentrated before testing. Since a large range of alkalinity is possible, a rough measurement is made initially using 0.1 M HCl titrant. This allows for adjusting sample size so that the titration volume is greater than 10 mL, but less than 50 mL. If for this sample the titrant volume used is very small, a 0.02 M HCl solution is used with an appropriate sample size. Thus, the “test titration” with 0.1 M HCl is a guess to see what concentration of acid is needed.

Use the following procedure:

A: Standardization

1. Prepare a 0.1 M sodium hydroxide solution. Quickly weigh about 4 g of sodium hydroxide pellets using a small beaker and transfer to a 1 L plastic bottle. Fill the bottle with 1 L of DI water and mix thoroughly. This solution will be standardized. (An alternative procedure is to dilute 8 g (about 5–6 mL) of 50% (w/w) sodium hydroxide to 1 L with DI water. This procedure eliminates sodium carbonate as an impurity since it is insoluble in the concentrated base.)

2. Prepare 0.1 M HCl (for alkalinity greater than 20 mg/L). In a fume hood, measure out 8.3 mL of concentrated HCl using a 10 mL graduated cylinder and dilute to 1 L in a glass or plastic bottle. Mix well.

3. Prepare 0.02 M HCl. Dilute 200 mL of the 0.1 M HCl to 1 L using volumetric flasks. Standardization of this solution may be done, but is not necessary. The HCl can be measured out with a graduated cylinder that can be calibrated, if necessary.

4. Standardize the 0.1 M NaOH against primary standard potassium acid phthalate (KHP). Weigh accurately (to 0.1 mg) three samples of KHP (previously dried) weighing about 0.5 g each (0.49–0.51 g). Quantitatively transfer the KHP to 250 mL Erlenmeyer flasks and dissolve in about 75 mL DI water. Add 3 drops of phenolphthalein indicator and titrate with the 0.1 M NaOH until the faintest pink persists for 30 seconds. The buret must be rinsed with three 10 mL portions of the sodium hydroxide before use.

5. Use the standardized 0.1 M NaOH solution to titrate 25.00 mL (pipetted) aliquots of the 0.1 M HCl diluted to about 75 mL with DI water. Do three determinations of the molarity of the HCl and use the average value in subsequent calculations. (An exercise at this point to get a feel for the number of trials needed to obtain a reasonable standard deviation is to continue titrating 25.00 mL aliquots and calculating the standard deviation after each measurement [after three] until a reasonable standard deviation is obtained. That is, if the average molarity is 0.102 then the standard deviation might be 0.003 M, and the relative standard deviation is about 3%.)

B: Indicator Titration for Alkalinity

1. Pipet 100 mL of sample (or the appropriate amount determined in a test titration) into a 250 mL Erlenmeyer flask. Add 3–5 drops of methyl orange.

2. Rinse a buret with three 10 mL portions of 0.1 M HCl. Fill with the acid and record the initial volume. Titrate the sample with the standardized 0.1 M HCl to the endpoint (which is orange to red), and record the final volume.
3. If the alkalinity is less than 20 mg/L, as determined by the test titration, use 0.02 M HCl and adjust the sample size if necessary. Titrate the sample as in Parts 1-2.
4. Do two additional titrations on the same sample according to Steps 1 and 2.
5. Repeat Steps 1-3 for a second type of environmental sample.

C: Potentiometric Titration

1. Calibrate the pH meter according to the procedure of Experiment 3.
2. Choose one of the environmental samples studied by the indicator titration to examine in this part of the experiment. Use a pipet to measure out the appropriate amount of sample into a 250 mL beaker. Lower the pH electrode into the sample, being certain that the bulb of the glass electrode is completely covered.
3. Using a magnetic stir bar and plate, obtain a potentiometric titration curve by adding standard 0.1 M HCl from a buret in either 0.5 mL or 1.0 mL increments, stirring and measuring the pH, until a pH of 4.0 is obtained. Record the pH after each addition of titrant.

Waste Minimization and Disposal

1. The water sample used for determining buffer capacity need not be collected from a polluted body of water and thus need not be hazardous waste. Otherwise, your instructor will direct you on the disposal method.
2. Extra hydrochloric acid and sodium hydroxide that needs to be disposed of can be used to neutralize one another. A final pH between 3 and 11 is needed before disposal in the laboratory drain. Standard acids and bases, however, might be used in later experiments and should not be disposed of before checking with the instructor.

Data Analysis

1. The molarity of sodium hydroxide is obtained from the stoichiometric titration reaction, $\text{NaOH} + \text{KHP} \longrightarrow \text{H}_2\text{O} + \text{KNaP}$. At the end point the moles of base are equal to the moles of acid. Also, $\text{mol NaOH} = [(\text{mL})/1000](\text{M})$ and $\text{mol KHP} = \text{mass}/\text{molar mass}$. Therefore, the molarity of NaOH is given by,

$$\text{M} = (\text{mass KHP} / 204.23) / (\text{mL NaOH} / 1000)$$

Report each individual molarity and the average of the values for NaOH.

2. Report the titration volumes and the calculated molarities of the 0.1 M HCl, and report the mean molarity.
3. If the 0.02 M HCl was used, report its molarity (from standardization or by calculation from the dilution of a standard solution).
4. The alkalinity for both the indicator and potentiometric methods is given by

$$[\text{Alk}] = \frac{1}{2}(\text{mL HCl})(M_{\text{HCl}}) (100.0 \text{ mg / mmol}) / \text{L of sample}$$

when the alkalinity is expressed in mg CaCO₃/L. The volume of titrant is the volume of HCl needed to achieve a pH of 4.3 and 100.0 mg/mmol is the molar mass of CaCO₃ (g/mol = mg/mmol).

- a) Report the alkalinity of the water sample that was done with one replicate. Report the individual values and the mean value. Compare with the potentiometric method done on the same sample.
 - b) Report the alkalinity for the second sample type done using the indicator method.
5. Compare the alkalinities for the two sample types and discuss their difference in terms of the sample site location.
 6. If Experiment 3 has been done, use the results for the potentiometric titration curve to obtain another value of the alkalinity, and include this value in the previous discussions.

Supplemental Activity

1. Total dissolved solids were determined in Experiment 1, and if the same samples are used in this experiment, it may be possible to determine if there is a relationship between dissolved solids and alkalinity. (In Experiment 8 the water hardness, which is partly due to calcium ions, will be determined. If the hardness is done using the same samples as in this experiment, it may be possible to relate the hardness to the alkalinity.)
2. Bottled spring water samples would make an interesting addition and comparison for this experiment.
3. It would be interesting to determine the pH of the samples studied in this experiment and list these values in a table with the determined alkalinities.

Questions and Further Thoughts

1. What is the difference between alkalinity and basicity?
2. Can an acidic solution have a measurable alkalinity? Explain with an example.
3. What is the difference between alkalinity and buffer capacity?

Notes

1. Sodium carbonate can be used to standardize the hydrochloric acid instead of using standard base.
2. A CBL (calculator-based laboratory) unit can be used to store pH data, which can then be downloaded to a computer to generate the potentiometric titration curve. Details about this procedure are given in the instructor's manual.
3. The density of 50% sodium hydroxide solution is 1.52 g/mL at room temperature.

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