
21

DETERMINATION OF ALKALINITY OF NATURAL WATERS

Purpose: To determine the alkalinity of a natural water sample by titration

BACKGROUND

Alkalinity is a chemical measurement of a water's ability to neutralize acids. Alkalinity is also a measure of a water's buffering capacity or its ability to resist changes in pH upon the addition of acids or bases. The alkalinity of natural waters is due primarily to the presence of weak acid salts, although strong bases may also contribute in industrial waters (i.e., OH^-). Bicarbonates represent the major form of alkalinity in natural waters and are derived from the partitioning of CO_2 from the atmosphere and the weathering of carbonate minerals in rocks and soil. Other salts of weak acids, such as borate, silicates, ammonia, phosphates, and organic bases from natural organic matter, may be present in small amounts. Alkalinity, by convention, is reported as mg/L CaCO_3 , since most alkalinity is derived from the weathering of carbonate minerals rather than from CO_2 partitioning with the atmosphere. Alkalinity for natural water (in molar units) is typically defined as the sum of the carbonate, bicarbonate, hydroxide, and hydronium concentrations such that

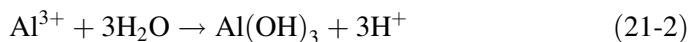
$$[\text{alkalinity}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}_3\text{O}^+] \quad (21-1)$$

Alkalinity values can range from zero from acid rain-affected areas, to less than 20 mg/L for waters in contact with non-carbonate-bearing soils, to 2000 to

4000 mg/L for waters from the anaerobic digestors of domestic wastewater treatment plants (Pohland and Bloodgood, 1963).

Neither alkalinity nor acidity, the converse of alkalinity, has known adverse health effects, although highly acidic or alkaline waters are frequently considered unpalatable. However, alkalinity can be affected by or affect other parameters. Below are some of the most important effects of alkalinity.

1. The alkalinity of a body of water determines how sensitive that water body is to acidic inputs such as acid rain. A water with high alkalinity better resists changes in pH upon the addition of acid (from acid rain or from an industrial input). We discuss this further when we discuss the relevant equilibrium reactions.
2. Turbidity is frequently removed from drinking water by the addition of alum, $\text{Al}_2(\text{SO}_4)_3$, to the incoming water followed by coagulation, flocculation, and settling in a clarifier. This process releases H^+ into the water through the reaction



For effective and complete coagulation to occur, alkalinity must be present in excess of that reacted with the H^+ releases. Usually, additional alkalinity, in the form of $\text{Ca}(\text{HCO}_3)_2$, $\text{Ca}(\text{OH})_2$, or Na_2CO_3 (soda ash), is added to ensure optimum treatment conditions.

3. Hard waters are frequently softened by precipitation methods using CaO (lime), Na_2CO_3 (soda ash), or NaOH . The alkalinity of the water must be known in order to calculate the lime, soda ash, or sodium hydroxide requirements for precipitation.
4. Maintaining alkalinity is important to corrosion control in piping systems. Corrosion is of little concern in modern domestic systems, but many main water distribution lines and industrial pipes are made of iron. Low-pH waters contain little to no alkalinity and lead to corrosion in metal pipe systems, which are costly to replacement.
5. Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) can complex other elements and compounds, altering their toxicity, transport, and fate in the environment. In general, the most toxic form of a metal is its uncomplexed hydrated metal ion. Complexation of this free ion by carbonate species can reduce toxicity.

THEORY

As mentioned previously, alkalinity in natural water is due primarily to carbonate species. The following set of chemical equilibria is established:



where H_2CO_3^* represents the total concentration of dissolved CO_2 and H_2CO_3 . Reaction (21-3) represents the equilibrium of CO_2 in the atmosphere with dissolved CO_2 in the water. The equilibrium constant, using Henry's law, for this reaction is

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} = 4.48 \times 10^{-5} \text{ M/mmHg} \quad (21-6)$$

The equilibrium expressions for reactions (21-4) and (21-5) are

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{-6.37} \quad (21-7)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.32} \quad (21-8)$$

As you can see from equations (21-6) to (21-8), the important species contributing to alkalinity are CO_3^{2-} , HCO_3^- , and H_2CO_3 , and each of these reactions is tied strongly to pH. To illustrate the importance of these relations, we will calculate the pH of natural rainwater falling through Earth's atmosphere that currently contains 380 ppm CO_2 .

First, we convert the concentration of CO_2 in the air to mol/L (step 1), and then calculate its partial pressure for use in equation (21-6) (step 2). This enables us to calculate the molarity of carbon dioxide in water [the $[\text{H}_2\text{CO}_3]$ term in equation (21-6)] (step 3), and then the molarity of H_2CO_3 in the water (step 4). Finally, we calculate the pH of the water, based on the equilibrium established between the different species of dissolved carbonate (step 4).

Step 1:

$$\begin{aligned} \text{density of air} &= 0.001185 \text{ g/mL}(1000 \text{ mL/L}) = 1.185 \text{ g/L} \\ \text{CO}_2(\text{air}) &= 380 \text{ mg CO}_2/\text{kg air} \\ &= 380 \text{ mg CO}_2/\text{kg air}(1 \text{ kg air}/1000 \text{ g air})(1.185 \text{ g/L}) \\ &= 0.450 \text{ mg CO}_2/\text{L} \\ &= 0.450 \text{ mg/L}(1 \text{ g}/1000 \text{ mg})(1 \text{ mol CO}_2/44 \text{ g CO}_2) \\ &= 1.02 \times 10^{-5} \text{ M CO}_2 \text{ in air} \end{aligned}$$

Step 2: Using $PV = nRT$ (note that $n/V = M$) gives us

$$\begin{aligned} P_{\text{CO}_2} &= MRT = (1.02 \times 10^{-5} \text{ mol/L})(0.08206 \text{ L} \cdot \text{M}/\text{mol} \cdot \text{K})(298.14 \text{ K}) \\ &= 2.50 \times 10^{-4} \text{ atm} \end{aligned}$$

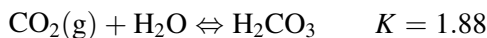
Step 3: Using $K_{\text{CO}_2} = [\text{CO}_2]_{\text{H}_2\text{O}}/P_{\text{CO}_2} = 4.48 \times 10^{-5} \text{ M/mmHg}$ yields

$$P_{\text{CO}_2}(\text{mmHg}) = 2.50 \times 10^{-4} \text{ atm } (760 \text{ mmHg/atm}) = 0.19 \text{ mmHg}$$

$$K_{\text{CO}_2} = 4.48 \times 10^{-5} \text{ M/mmHg} = M_{\text{CO}_2}/P_{\text{CO}_2}$$

$$\begin{aligned} M_{\text{CO}_2} \text{ in water} &= 4.48 \times 10^{-5} \text{ M/mmHg } (0.19 \text{ mmHg}) \\ &= 8.52 \times 10^{-6} \text{ M CO}_2 \end{aligned}$$

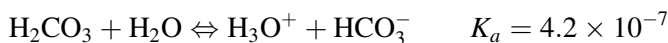
Step 4: From step 3, $\text{CO}_2(\text{aq}) = 8.52 \times 10^{-6} \text{ M}$;



$$K = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2(\text{aq})]}$$

$$\begin{aligned} [\text{H}_2\text{CO}_3] &= 1.88(8.52 \times 10^{-6} \text{ M}) \\ &= 1.6 \times 10^{-5} \text{ M H}_2\text{CO}_3 \end{aligned}$$

Step 5: Now, solving for pH using the equilibrium expression for H_2CO_3 , we obtain



$$K_a = 4.2 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$4.2 \times 10^{-7} = \frac{x^2}{1.6 \times 10^{-5} - x}$$

and using the quadratic equation to solve for x yields

$$x = [\text{H}_3\text{O}^+] = 2.59 \times 10^{-6}$$

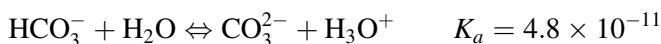
$$\text{pH} = 5.59 \quad \text{pH of natural rainwater}$$

We can also solve for the remaining chemical species using equilibrium equations.

$$[\text{HCO}_3^-] = x \text{ also, so } [\text{HCO}_3^-] = 2.59 \times 10^{-6} \text{ M HCO}_3^-$$

$$[\text{H}_2\text{CO}_3] = 1.6 \times 10^{-5} (\text{total carbonic concentration})$$

$$- 2.59 \times 10^{-6} = 1.3 \times 10^{-5} \text{ M}$$



$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

Summarizing yields

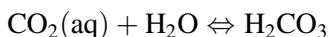
$$[\text{H}_3\text{O}^+] = 2.59 \times 10^{-6} \text{ M} \quad \text{pH} = 5.59$$

$$[\text{H}_2\text{CO}_3] = 1.6 \times 10^{-5} \text{ M}$$

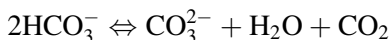
$$[\text{HCO}_3^-] = 2.59 \times 10^{-6} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.88 \times 10^{-11} \text{ M}$$

Thus, a pH value of less than 5.6 for a rain or snow sample is due to mineral acids from atmospheric pollution or volcanic emissions. Interaction of less acidic precipitation with soil minerals usually adds alkalinity and raises the pH value, which counteracts the use of carbon dioxide by algae during daylight hours. If the consumption rate of CO_2 is greater than its replacement rate from the atmosphere, as can occur when acid precipitation is input, the dissolved CO_2 concentration in the surface water and groundwater will fall and result in a shift to the left for the corresponding equilibrium reactions:



This will also result in an increase in the pH of the water. As the pH continues to increase, the alkalinity changes chemical species to replace the CO_2 consumed by the algae. Note the equilibrium shifts toward increased CO_2 concentrations, which is illustrated in the following reactions



It should be noted that even though we are creating hydroxide alkalinity, the total alkalinity has not changed, merely shifted in chemical form. We define *hydroxide alkalinity* later as alkalinity in excess of a pH value of 10.7. Algae can continue to consume CO_2 until the pH of the water has risen to between 10 and 11, when a growth inhibitory pH is reached and algae consumption of CO_2 is halted. This can result in a diurnal shift in the pH of the photic zone of a water body. In waters containing significant calcium concentrations, the set of reactions above can result in the precipitation of CaCO_3 on leaves and twigs in water, and in the long term, can lead to the formation of marl deposits in sediments. Thus, even algae can produce the industrial-sounding “hydroxide alkalinity.”

REFERENCES

American Water Works Association, *Standard Methods for the Examination of Water and Wastewater* 18th ed., AWWA, Denver, CO, 1992.

- Harris, D. C., *Quantitative Chemical Analysis*, 5th ed., W. H. Freeman, New York, 1998.
- Keith, L. H., *Compilation of EPA's Sampling and Analysis Methods*, Lewis Publishers, Chelsea, MI, 1992.
- Pohland, F. G. and D. E. Bloodgood, *J. Water Pollut. Control Fed.*, **35**, 11 (1963).
- Snoeyink, V. L. and D. Jenkins, *Water Chemistry*, Wiley, New York, 1980.
- Sawyer, C. N. and P. L. McCarty, *Chemistry for Environmental Engineering*, 3rd ed., McGraw-Hill, New York, 1978.
- Stumm W. and J. J. Morgan, *Aquatic Chemistry*, 3rd ed., Wiley, New York, 1995.

IN THE LABORATORY

To determine the alkalinity, a known volume of water sample is titrated with a standard solution of strong acid to a pH value of approximately 4 or 5. Titrations can be used to distinguish between three types of alkalinity: hydroxide, carbonate, and bicarbonate alkalinity. Carbonate alkalinity is determined by titration of the water sample to the phenolphthalein or metacresol purple indicator endpoint, approximately pH 8.3. Total alkalinity is determined by titration of the water sample to the endpoint of the methyl orange, bromocresol green, or bromocresol green–methyl red indicators, approximately pH 4.5. The difference between the two is the *bicarbonate alkalinity*. *Hydroxide* (OH^-) *alkalinity* is present if the *carbonate*, or phenolphthalein, *alkalinity* is more than half of the total alkalinity [American Water Works Association (AWWA), 1992]. Thus, the hydroxide alkalinity can be calculated as two times the phenolphthalein alkalinity minus the total alkalinity.

Note that only approximate pH values can be given for the final endpoint, which occurs near a pH value of 4.5. This is because the exact endpoint at the end of the titration, the *equivalence point*, is dependent on the total concentration of carbonate species in solution, while the indicator color change is referred to as the *endpoint*. The endpoint is subject to the pH value only where the indicator changes color and is not influenced by the total alkalinity in solution, whereas the equivalence point is inversely related to alkalinity, with higher total alkalinity corresponding to equivalence at a lower pH value. This can be explained by looking at a pC–pH diagram of the carbonate system. A pC–pH exercise is included in this manual (Chapter 23), and a pC–pH program is included on the accompanying CD-ROM. Figure 21-1 is for a 0.0010 *M* total carbonate system. The exact equivalence point for the alkalinity titration occurs when the H^+ concentration equals the HCO_3^- concentration. For the 0.001 *M* carbonate solution (Figure 21-1), this corresponds to the location of the arrow at pH 4.67. As the carbonate concentration increases to 0.10 *M* (Figure 21-2), the carbonate species lines shift to yield an interception at a pH value of 3.66. This is a significant difference in equivalence points but is not reflected in the indicator endpoint. As a result, the equivalence points described below have been suggested. The following endpoints, corresponding to total alkalinity concentrations, are suggested in AWWA (1992): pH 5.1 for total alkalinities of about 50 mg/L, pH 4.8 for 150 mg/L, and pH 4.5 for 500 mg/L.

Two points should be noted about the titration curve (again, refer to the pC–pH diagrams in Figures 21-1 and 21-2).

1. At pH 10.7, the $[\text{HCO}_3^-]$ equals the $[\text{OH}^-]$. This is called an equivalence point and is the endpoint of the caustic alkalinity and total acidity titrations. At pH 8.3, the $[\text{H}_2\text{CO}_3]$ equals the $[\text{CO}_3^{2-}]$. This is the endpoint for carbonate alkalinity and CO_2 acidity titrations. In the alkalinity titration virtually all of the CO_3^{2-} has reacted (thus, the term *carbonate alkalinity*) and half of the HCO_3^- has reacted at the endpoint.

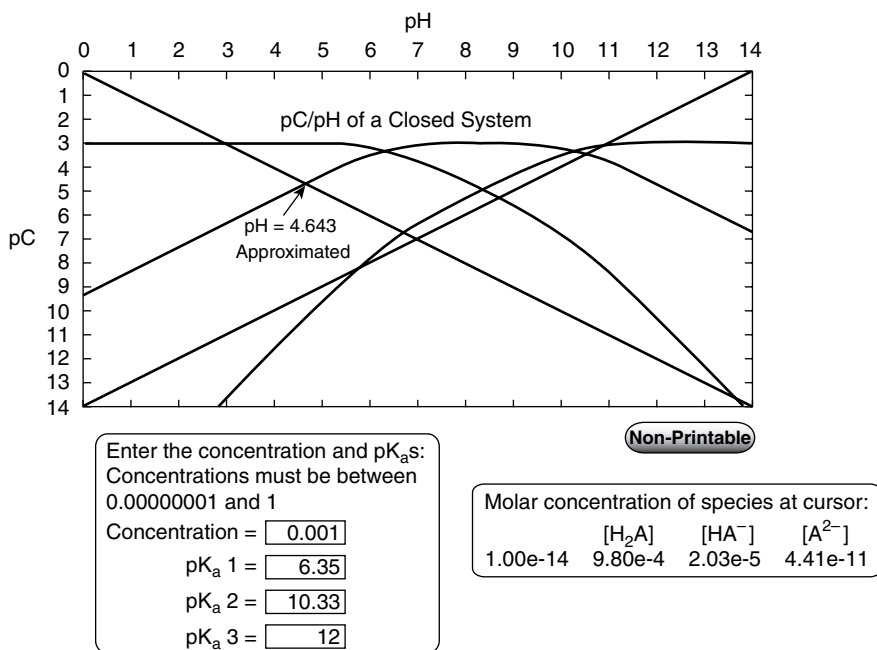


Figure 21-1. pC–pH diagram for a 0.001 M carbonate solution. Refer to and use the pC–pH simulator, which will give color lines on the plot.

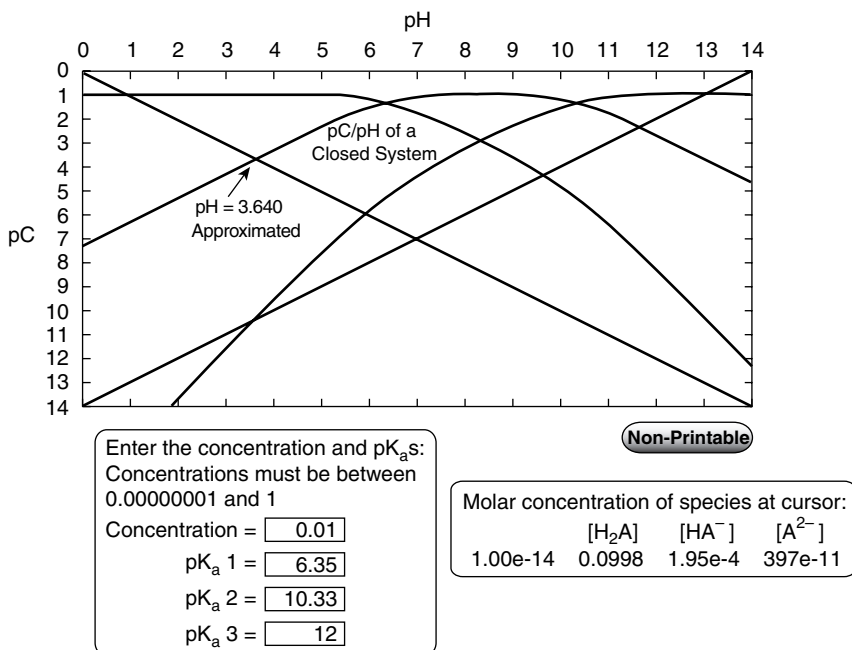


Figure 21-2. pC–pH diagram for a 0.10 M carbonate solution. Refer to and use the pC–pH simulator, which will give color lines on the plot.

2. At pH ~ 4.5 (dependent on the total alkalinity), the $[\text{H}^+]$ equals the $[\text{HCO}_3^-]$. This is the endpoint for mineral acidity and total alkalinity titrations.

Safety Precautions

- As in all laboratory exercises, safety glasses must be worn at all times.
- Avoid skin and eye contact with NaOH and HCl solutions. If contact occurs, rinse your hands and/or flush your eyes for several minutes. Seek immediate medical advice for eye contact.
- Use concentrated HCl in the fume hood and avoid breathing its vapor.

Chemicals and Solutions

Sample Handling. Alkalinity is a function of the dissolved CO_2 in solution. Thus, any chemical or physical manipulation of the sample that will affect the CO_2 concentration should be avoided. This includes filtering, diluting, concentrating, or altering the sample in any way. Nor should the sampling temperature be exceeded, as this will cause dissolved CO_2 to be released. Samples containing oil and grease should be avoided. Sampling and storage vessels can be plastic or glass without headspace.

- *Sodium carbonate solution*, $\sim 0.025\text{ M}$. Primary standard grade Na_2CO_3 must be dried for 3 to 4 hours at 250°C and be allowed to cool in a desiccator. Weigh 0.25 g to the nearest 0.001 g and quantitatively transfer all of the solid to a 100-mL volumetric flask. Dilute to the mark with distilled or deionized water. Calculate the exact molarity of the solution in the 100-mL flask.
- *Standardized hydrochloric acid* (about 0.02 M). Add 8.3 mL of concentrated (12 M) HCl to a 1000-mL volumetric flask and dilute to the mark with deionized or distilled water. This solution has a molarity of approximately 0.10 M . Transfer 200 mL of this solution to another 1000-mL volumetric flask to prepare the 0.020 M solution. Standardize the dilute HCl solution (about 0.020 M) against the Na_2CO_3 primary standard solution. This is done by pipetting 10.00 mL of the $\sim 0.025\text{ M}$ Na_2CO_3 solution into a 250-mL Erlenmeyer flask and diluting to about 50 mL with distilled or deionized water. Add 3 to 5 drops of the bromocresol green indicator (more if needed) to the Erlenmeyer flask and titrate with $\sim 0.02\text{ M}$ HCl solution. Bromocresol green changes from blue to yellow as it is acidified. The indicator endpoint is intermediate between blue and yellow, and appears as a distinct green color. Determine the molarity of the HCl solution. Remember to wash down any droplets of solution from the walls of the flask.
- *Bromocresol green indicator solution*, about 0.10%, pH 4.5 indicator. Dissolve 0.100 g of the sodium salt into 100 mL of distilled or deionized water. Colors: yellow in acidic solution, blue in basic solution.

- *Phenolphthalein solution*, alcoholic, pH 8.3 indicator. Colors: colorless in acidic solution, red in basic solution.
- *Metacresol purple indicator solution*, pH 8.3 indicator. Dissolve 100 mg of metacresol purple in 100 mL of water. Colors: yellow in acidic solution, purple in basic solution.
- *Mixed bromocresol green–methyl red indicator solution*. You may use either the water- or alcohol-based indicator solution. Water solution: dissolve 100 mg of bromocresol green sodium salt and 20 mg of methyl red sodium salt in 100 mL of distilled or deionized water. Ethyl or isopropyl alcohol solution: dissolve 100 mg of bromocresol green and 20 mg of methyl red in 100 mL of 95% alcohol.

Glassware

- Standard laboratory glassware: 50-mL buret, 250-mL Erlenmeyer flasks, 50-mL beakers, Pasteur pipets

PROCEDURE

Limits of the Method. Typically, 20 mg of CaCO_3/L . Lower detection limits can be achieved by using a 10-mL microburet (Keith, 1992)

1. First, an adequate sample volume for titration must be determined. This is accomplished by performing a test titration. Select a volume of your sample, such as 100 mL, and titrate it to estimate the total alkalinity of your sample. For best accuracy, you should use at least 10 mL but not more than 50 mL from a 50-mL buret. Adjust your sample size to meet these criteria.
2. Titrate your sample with standardized 0.02 *M* HCl solution. Add phenolphthalein or metacresol purple indicator solution and note the color change around a pH value of 8.3. Alternatively, a pH meter can be used to determine the inflection point. This measurement will be a combination of the hydroxide and carbonate alkalinity.
3. Continue the titration to the ~ 4.5 endpoint by adding bromocresol green or the mixed bromocresol green–methyl red indicator solution. Better results will be obtained by titrating a new sample to the ~ 4.5 endpoint. This will avoid potential color interferences between the 8.3 and 4.5 pH indicators. Note the color change near a pH value of 4.5. Alternatively, a pH meter can be used to determine the inflection point.
4. Repeat steps 2 and 3 at least three times (excluding the trial titration to determine your sample volume).
5. Calculate the hydroxide, carbonate, bicarbonate, and total alkalinities for your samples. Report your values in mg CaCO_3/L . Show all calculations in your notebook.

Waste Disposal

After neutralization, all solutions can be disposed of down the drain with water.

ADVANCED STUDY ASSIGNMENT

1. In your own words, define *alkalinity* and explain why it is important in environmental chemistry.
2. What are the primary chemical species responsible for alkalinity in natural waters?
3. Alkalinity can be expressed in three forms: hydroxide alkalinity, carbonate alkalinity, and total alkalinity. Each of these is determined by titration, but at different pH values. What is the approximate endpoint pH for the carbonate alkalinity titration? What is the approximate endpoint pH for the total alkalinity titration?
4. Why can we give only approximate pH endpoints for each type of alkalinity?
5. To prepare yourself for the laboratory exercise, briefly outline a procedure for titrating a water sample for alkalinity. (List the major steps.)
6. If you titrate 200 mL of a sample with 0.0200 *M* HCl and the titration takes 25.75 mL of acid to reach the bromocresol green endpoint, what is the total alkalinity of the sample?
7. The atmospheric concentration of CO₂ is predicted to increase up to 750 ppm by the year 2100. What will be the pH of rainwater if it is in equilibrium with an atmosphere containing 500 ppm CO₂?