MP 2 Case Study 8 - Greenhouse Gases and Rainwater

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1 Background

Civil engineering is a broad field that includes such diverse areas as structural, geotechnical, transportation, water-resources, and environmental engineering. The last area has traditionally dealt with pollution control. However, in recent years, environmental engineers (as well as chemical engineers) have addressed broader problems such as climate change.

It is well documented that the atmospheric levels of several *greenhouse gases* has been increasing over the past 50 years. For example, Fig. 1 shows data for the partial pressure of carbon dioxide (CO_2) collected at Mauna Loa, Hawaii from 1958 through 2003. The trend in the data can be nicely fit with a quadratic polynomial,

$$p_{CO_2} = 0.011825(t - 1980.5)^2 + 1.356975(t - 1980.5) + 339 \tag{1}$$

where p_{CO_2} = the partial pressure of CO_2 in the atmosphere [ppm]. The data indicates that levels have increased over 19% during the period from 315 to 376 ppm.

Aside from global warming, greenhouse gases can also influence atmospheric chemistry. One question that we can address is how the carbon dioxide trend is affecting the pH of rainwater. Outside of urban and industrial areas, it is well documented that carbon dioxide is the primary determinant of the pH of the rain. pH is the measure of the activity of hydrogen ions and, therefore, its acidity. For dilute aqueous solutions, it can be computed as

$$pH = -\log_{10}[H^+] \tag{2}$$

where $[H^+]$ is the molar concentration of hydrogen ions.

The following five nonlinear system of equations govern the chemistry of rainwater.

$$K_1 = 10^6 \frac{[H^+][HCO_3^-]}{K_H p_{CO_2}} \tag{3}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{HCO_3^-} \tag{4}$$

$$K_w = [H^+][OH^-] \tag{5}$$

$$c_T = \frac{K_H p_{CO_2}}{10^6} + [HCO_3^-] + [CO_3^{2-}] \tag{6}$$

$$0 = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{7}$$

where K_H = Henry's constant, and K_1, K_2 and K_w are equilibrium coefficients. The five unknowns are c_T = total inorganic carbon, $[HCO_3^-]$ = bicarbonate, $[CO_3^{2-}]$= carbonate, $[H^+]$ = hydrogen ion, and $[OH^-]$ = hydroxyl ion. Notice how the partial pressure of CO_2 shows up in Eqs. (3) and (6).

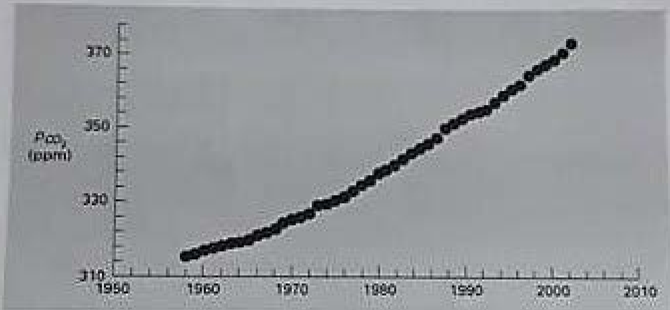

Figure 1: Average annual partial pressures of atmospheric carbon dioxide (ppm) measured at Mauna Loa, Hawaii

1.1 Tasks

1. What does "partial pressure of a gas" mean?
2. Check to see if a java class from our Git repo for plotting exists in our Git data
3. Use the java class from our Git repo to plot Eq. (1) and obtain a graph similar to Fig. 1. create one if the class does not yet exist in our repo
4. Discuss briefly what an inorganic carbon is? Use pictures.
5. Discuss briefly what bicarbonates are? Use pictures.
6. Discuss briefly what carbonates are? Use pictures.
7. What other green-house gases are there?
8. How are the activities of man releasing significant amounts of green house gases in the atmosphere.

2 Problem Proper

Use these equations to compute the pH of rainwater given that $K_H = 10^{-1.46}$, $K_1 = 10^{-6.3}$, $K_2 = 10^{-10.3}$, and $K_w = 10^{-14}$. Compare the results in 1958 when the p_{CO_2} was 315 and in 2003 when it was 375 ppm. When selecting a numerical method for your computation, consider the following:

- You know with certainty that the pH of rain in pristine areas always falls between 2 and 12
- You also know that your measurement devices can only measured pH to two places of decimal precision.

2.1 Tasks

1. What root finding techniques exist in our Git repo?
2. Given the precision of the data, how many decimal places should be reasonable to compute for?

3. What does an acidity of pH=2 mean in practical terms?

4. What does a pH=12 mean in practical terms?

5. What can you say to kids showering in the rain based on what you researched?

3 Solution

3.1 Solution Strategy

There are a variety of ways to solve this nonlinear system of five equations. One way is to eliminate unknowns by combining them to produce a single function that only depends on $[H^+]$. To do this, first solve Eqs. (3) and (4) for

$$[HCO_3^-] = \frac{K_1}{10^6[H^+]}K_H p_{CO_2} \tag{8}$$

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} \tag{9}$$

Substitute Eq. (8) into (9)

$$[CO_3^{2-}] = \frac{K_2K_1}{10^6[H^+]^2}K_H p_{CO_2} \tag{10}$$

Equations (8) and (10) can be substituted along with Eq. (5) into Eq. (7) to give

$$0 = \frac{K_1}{10^6[H^+]}K_H p_{CO_2} + 2\frac{K_2K_1}{10^6[H^+]^2}K_H p_{CO_2} + \frac{K_w}{[H^+]} - [H^+] \tag{11}$$

Although it might not be apparent, this result is a third-order polynomial in $[H^+]$. Thus, its root can be used to compute the pH of the rainwater.

3.2 Tasks

1. Derive Eq. (11)
2. Algebraically manipulate Eq. (11) to show that it is a third-order polynomial in $[H^+]$.

3.3 Numerical Method

Now we must decide which numerical method to employ to obtain the solution. There are two reasons why bisection would be a good choice. First, the fact that the pH always falls within the range from 2 to 12, provides us with two good initial guesses. Second, because the pH can only be measured to two decimal places of precision, we will be satisfied with an absolute error of $E_{a,d} = 0.005$. Remember that given an initial bracket and the desired relative error, we can compute the number of iterations *a priori*. The result is n = log2(10)/0.005 = 10.9658. Thus, eleven iterations of bisection will produce the desired precision.

If this is done, the result for 1958 will be a pH of 5.6279 with a relative error of 0.0868%. We can be confident that the rounded result of 5.63 is correct to two decimal places. This can be verified by performing another run with more iterations. For example, if we perform 35 iterations, a result of 5.6304 is obtained with an approximate relative error of $\varepsilon_a = 5.17 \times 10^{-8}\%$. The same calculation can be repeated for the 2003 conditions to give pH = 5.59 with $\varepsilon_a = 0.0874\%$.

Interestingly, these results indicate that the 19% rise in atmospheric CO_2 levels has produced only a 0.67% drop in pH. Although this is certainly true, remember that the pH represents a logarithmic scale as defined by

$$pH = -\log_{10}[H^+]$$

where [H+] is the molar concentration of hydrogen ions.

Consequently, a unit drop in pH represents a 10-fold increase in hydrogen ion. The concentration can be computed as $[H+] = 10^{-pH}$ and the resulting percent change can be calculated as 9.1%. Therefore, the hydrogen ion concentration has increased about 9%.

There is quite a lot of controversy related to the true significance of the greenhouse gas trends. However, regardless of the ultimate implications, it is quite sobering to realize that something as large as our atmosphere has changed so much over a relatively short time period. This case study illustrates how numerical methods can be employed to analyze and interpret such trends. Over the coming years, engineers and scientists can hopefully use such tools to gain increased understanding and help rationalize the debate over their ramifications.

3.4 Tasks

1. Check the Java Git repo for a bisection class. If none is found, make one for the repo.
2. Use the bisection code and do 12 iterations of bisection to solve the problem and record the results in an iteration table.
3. Look at the results for iteration #12 and briefly explain why it is unnecessary in achieving the desired precision.
4. Likewise, look for Regula Falsi and Secant classes in our Git repo. Create them if they don't exist yet.
5. Expand your iteration table to include 12 iterations of Regula Falsi and Secant results.
6. Explain the differences among the results.
7. How many iterations of each root finding technique would have been needed to achieve the desired precision?
8. Research and briefly discuss he latest findings with regard to climate change.
9. Research and briefly discuss he latest activities in the Philippines with regard to climate change.