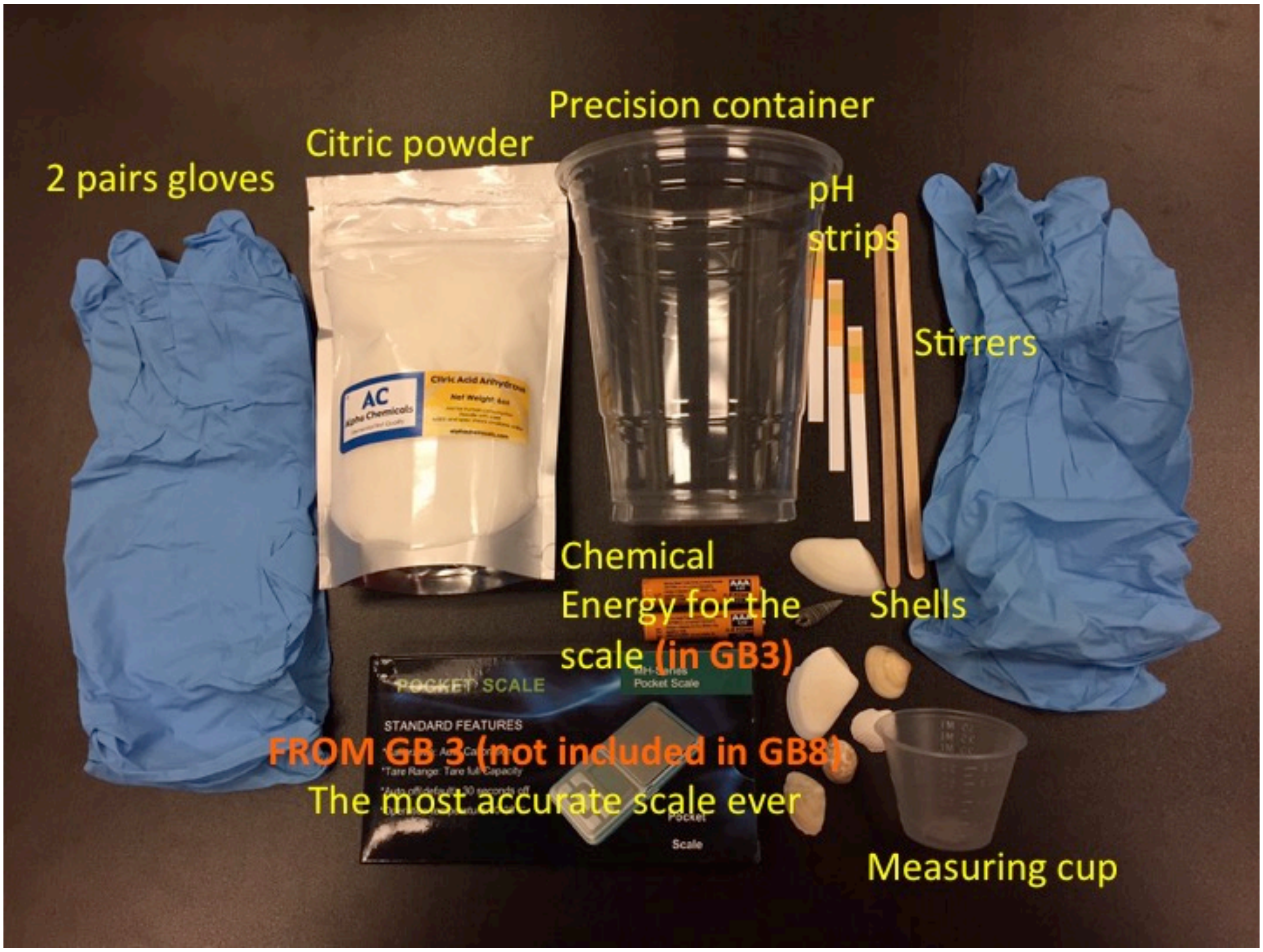
Goodie bag #8: Reactions

Handed out on 11.16.18 | Quiz #8.5 (NOT GRADED; take-home quiz on 11.20.18)

3.91
Do yourself a solid.

Please treat all contents of every Goodie Bag with care; remember that any item may be dangerous if improperly used. You are responsible for your own actions. Make sure to carry out any activities with items in this bag in an appropriate environment.



This bag contains:

- 6 oz of citric powder
- 1 precision container
- 1 measuring cup
- Beautiful shells (no sea animals were harmed)
- 3 pH strips with amazing zero-digit accuracy
- 2 pairs of nitrile gloves
- 2 stirrers

You will also need your scale and batteries handed out with GB3!
What to bring to the quiz: for this one, just your deep knowledge!

Introduction

This goodie bag will explore a chemical reaction in a low-pH environment, the reaction kinetics, rate law, and temperature dependence. We use seashells as a way to study reactions so that you can "touch and feel" the challenge of ocean acidification. As was mentioned in lecture, CO_2 emissions do not just cause a greenhouse effect leading to dramatic changes in climate. Here is a graphic that shows how CO_2 emissions will alter – via simple chemical reactions – the acidity of the ocean.

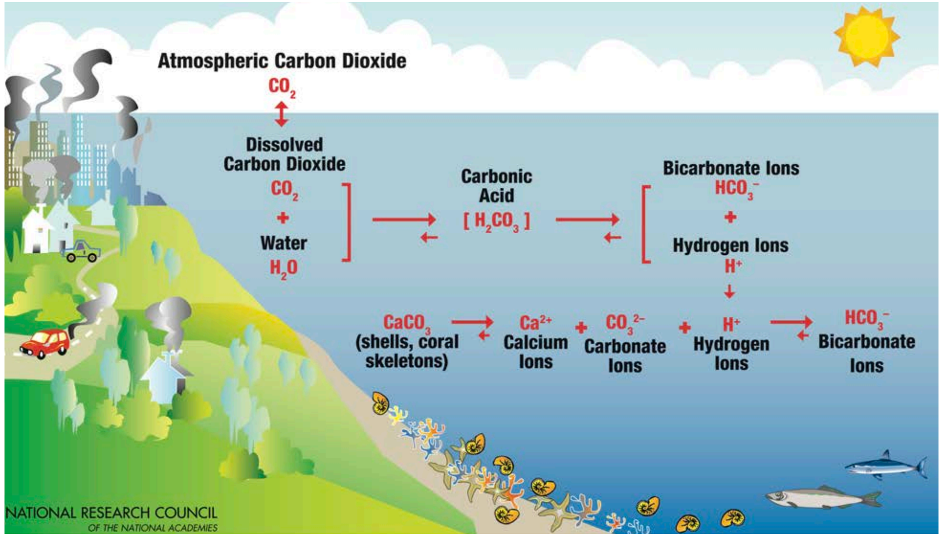
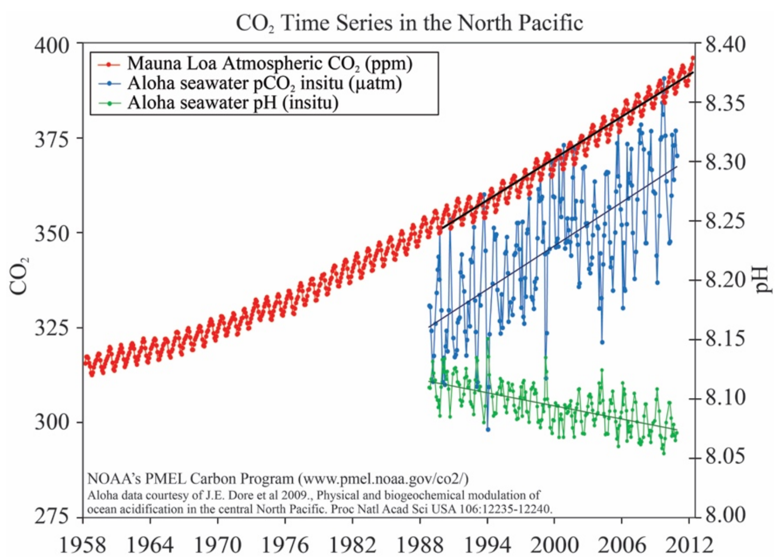


Diagram showing chemical processes as atmospheric carbon dioxide is absorbed into the ocean. Source: National Academy of Sciences. License: CC BY-NC.

Because of this chemistry, as the ocean absorbs more and more CO_2, it will also become more and more acidic. Below is a plot of the "traditional" CO_2 curve that most of us have seen, but now overlaid on top is the pH of the ocean (green data).



Courtesy of NOAA.

You can see that the drop in ocean pH so far doesn't seem like too much, from the historical value of pH=8.18 to the current value of pH=8.07. But remember that this is on a log scale and so represents an exponential change in the reaction chemistry! By 2100 the pH of the ocean will be pH=7.8 if we continue on our current track of CO_2 emissions. Why does this matter? Because the majority of the bottom of the food chain in the ocean is protected by calcium carbonate, or $CaCO_3$, or as we also call them, shells. As you can see in that first figure, with a more acidic environment the $CaCO_3$ will react and dissolve.

Here is what happens to a healthy pteropod (also called a "Sea Butterfly") when exposed to water with a pH of 7.8. Upper left is "normal ocean" which means the ocean of the past 50 million years (pH=8.18), while the sequence shows how over the course of only days the calcium carbonate shell dissolves in "future ocean" (pH=7.8). Even in current (pH=8.07) ocean, scientists are finding enormous decay in the shells protecting these creatures. Without the shells, they cannot survive. The pteropod is not only a crucial food source for marine life "up the chain", but because of its fragility, it also serves as a critical early warning to what is likely to happen to all shellfish.

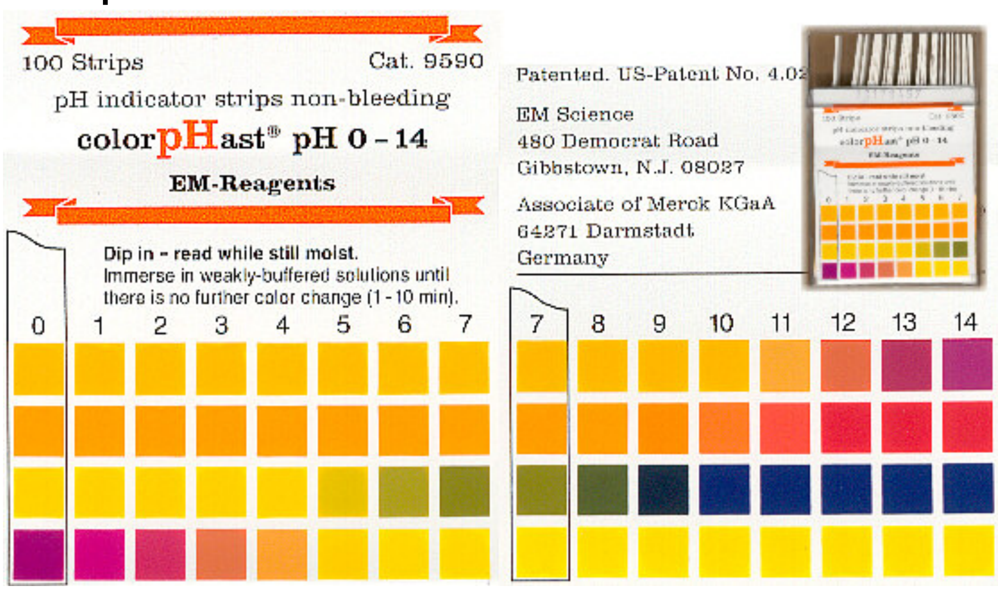
Dissolving pteropod © David Littschwager/ National Geographic Society via the [Smithsonian Institution](). All rights reserved. This content is excluded from our Creative Commons license. See https://ocw.mit.edu/fairuse.

The idea of this Goodie Bag is to have you get some hands-on exposure to reactions in the context of this urgent global crisis. Since the tiny pteropod weighs only about 0.01 mg and is 0.5 mm across, we'll instead use larger shells to carry out our experiments. We'll also lower the pH by considerably more than the oceans will ever get in order to accelerate the experiments so you can measure results in minutes as opposed to days or months. But as you watch those CO_2 bubbles form and the shell dissolve, note that this is the exact same reaction that is already happening to shells in the ocean, and will continue to happen at an alarming rate as CO_2 emission continue to rise unbounded.

NOTE: the citric powder is the same stuff that's in oranges, lemons, limes and other yummy foods. Still, the powder we provide here is not edible due to how it was produced, and not for consumption. Do NOT drink the solution. Wear the gloves when doing the experiment and just as when you're squeezing a lemon or lime, avoid any contact with eyes or anything that would be sensitive to it.

Instructions:

1. **Take your scale from GB3 and make sure it works. You should be able to get pretty good repeatability to the tenth of a gram for different objects.**
2. **RUN #1: take one of your shells and weigh it. You can also do several shells at the same time but keep enough to do a second run. Record the initial weight.**
3. **Put on a pair of the elegant nitrile gloves.**
4. **Take the large plastic cup and fill it with tap water about half-way.**
5. **Measure out 2 level scoops of the citric powder using the small but accurate measuring cup, and put it into the water. Stir well using the stirrer until all of the citric powder is fully dissolved (it may take a minute of stirring - the water should look pretty clear again).**
6. **Use a pH strip to measure the pH of the solution and record the value. Compare what you see in the strip with the chart shown below.**



7. **Have a timer ready, and place the shell(s) that you weighed into the low-pH solution. Note that spiral shells will float while non-spiral ones sink to the bottom. Either type of shell is fine. Record what you observe.**
8. **At time ~ 20 minutes, take out the shell with the gloves on and record the exact time. Let the shell dry for a bit (maybe even ½ hour or so) before you weigh it again. Make sure to wait until the measured weight of the shell is stable over ~3-4 minutes, as this will make sure all the water has evaporated. Record the new weight of the shell.**
9. **Place the shell(s) back into the solution and repeat steps 7-8 once more. This gives you a total of three mass measurements, at reaction times = 0, ~20, and ~40 minutes (the time in-between when drying doesn't count since no reaction is occurring).**
10. **RUN #2: Use either warmer or colder water (you can use ice to make it cold, or hot water from the tap to make it warm). Repeat steps 2-9.**
    Tip: you don't have to do this but if you want you can use a "bath" to keep your water cold/hot longer, that is, put the cup itself inside a bowl and fill the bowl with cold/hot water, so that it surrounds the cup.

Questions [note: Question 3 will not be tested on the quiz but could be on the exam)

Question 1: Reaction rate, order, and rate constant

a) Plot your data for RUN #1 as shell mass (g) vs. time (s). What do you observe? Convert the mass loss by the shell into a concentration of calcium carbonate ($CaCO_3$) in solution. You can do this by computing the number of moles of $CaCO_3$ and assuming you have 0.2 liters of water. What is the order of the reaction?

b) What is the rate of the reaction? What is the rate constant for the reaction? What units does it have?

Question 2: Temperature dependence

a) Plot the same data as in Question 1 for RUN #2. What changed? Did the reaction rate change? Did the order of the reaction change? Compute the rate constant for the reaction in RUN #2.

b) As was discussed in lecture, you can use an Arrhenius relationship to correlate rate constant with temperature. Use this relationship, the rate constants from above, and estimates of the temperatures (for example, 20C and 5C) to compute the energy barrier for the $CaCO_3$ reaction. Assume the frequency factor (the constant in front of the exponential term) is independent of temperature.

Question 3: Fun with pH

a) You measured the pH of the citric powder solution using a pH strip. Let's calculate that pH and compare with what you measured. The reaction of the citric powder with water is as follows:

$$C_6H_8O_7 + H_2O \leftrightarrow C_6H_7O_7^- + H^+$$

Given that the acid dissociation constant for citric acid is $K_a = 7x10^{-4}$, use the concentrations to compute the pH of your solution. Assume that you mixed 0.06 g of $C_6H_8O_7$ with 0.2 liters of H_2O. Does your computed pH value agree with what you measured?

b) What would happen to the pH of your solution if you let it sit out for a few hours without any shells in it? (You can test this yourself if you want). Why would this (did this) happen? (hint: CO_2).

c) One possible solution to solve ocean acidification could be to add a base that counteracts the CO_2 dissolution. This is probably a very bad idea, as the ocean is a complex reaction mixture, with thousands of different chemical components. Adding NaOH wouldn't just raise the pH, it would also cause precipitation of thousands of other compounds (these drastic changes would most likely not be good for marine life or human ocean-going vessels). Even if this wasn't a problem, a second problem is related to just how much NaOH would be necessary to neutralize the entire ocean. Assuming that NaOH completely dissociates in water, each OH^- neutralizes 1 H^+ ion, and the ocean is 1.35 billion km^3 ($1.35 \cdot 10^{21}$ L), what mass of NaOH would you need to add to counteract the current pH change in the ocean from 8.07 back up to 8.18?

