Unit Acid-Base Chemistry
Ocean Acidification Laboratory
Pacific School of Innovation and Inquiry

## Felix Autenrieth

Master of Science in the Teaching of Chemistry Pre-Service Teacher

## Part A: Carbonic Acid and $\mathrm{CO}_{2}$ Equilibrium

$\frac{\text { https://serc.carleton.edu/eslabs/carbon/7a.html }}{\mathbf{H}^{*} \text { Ion }}$


## Equilibrium 1:

$\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{CO}_{3}$
What are the physical states of $\mathrm{CO}_{2}$ on Earth, Mars and Venus?

How can you shift the $\mathrm{CO}_{2}$ equilibrium?
Please think about real life examples

## Equilibrium 2:

$\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons$ $\mathrm{HCO}_{3}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$ The Ka of $\mathrm{H}_{2} \mathrm{CO}_{3}$ is: $4.47 \times 10^{-7}$

What is the pH range of the resulting Hydrocarbonic Acid solution?

How can you change the pH value?

## Materials you will need for your group:

- 200 ml beaker, flask, or similar size clear glass
- pH meter
- 3 test tubes
- A jar with sea water (from the Salish Sea)
- A jar with tap water
- A jar with diluted acetic acid (vinegar $1-2 \%$ )

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- Drinking straw
- 50 ml of Bromothymol Blue (BTB) in solution
- A source of $\mathrm{CO}_{2}$ - you!


## Follow this procedure:

1. With the pH meter measure the pH of the three water jars and note the values.
2. Pour 50 ml of the provided BTB solution into the beaker. Make note of its color.
3. Fill your 3 test tubes with the 3 different water samples from the jars (leave enough space to add BTB solution)
4. Mix enough BTB solution with your test tubes that you can see distinct colors as depicted in the picture below. Make of the color of each test tube.
5. Exhale your $\mathrm{CO}_{2}$ through the straw into each test tube. Make sure you don't "suck up" any of the BTB solution into your straw and mouth.
6. When a color change has occurred, stop exhaling $\mathrm{CO}_{2}$ into the straw. Compare your color change to the image below. Note any color changes from before.
7. Measure the pH value of the test tubes after you have inhaled $\mathrm{CO}_{2}$.


> Bromothymol Blue (BTB) pH indicator dye in an acidic, neutral, and basic (alkaline) solution - left to right.

Does a change in dissolved $\mathrm{CO}_{2}$ cause a change in pH ? What's the evidence?

With the pH scale diagram explain the pH change atomistically? Do you consider that change large or small?

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## The Keeling Curve - An Important Science Graph - Why?

Latest $\mathrm{CO}_{2}$ reading
April 27, 2015
402.92 ppm

Carbon dioxide concentration at Mauna Loa Observatory


Reference: https://serc.carleton.edu/eslabs/carbon/7a.html

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## Part B: Ocean Acidification in a Cup

## https://www.exploratorium.edu/snacks/ocean-acidification-in-cup

## Change the atmosphere to change the water below

Create a carbon dioxide-rich atmosphere in a cup and watch how it changes the water beneath it. This model of ocean-atmosphere interaction shows how carbon dioxide gas diffuses into water, causing the water to become more acidic. Ocean acidification is a change that can have big consequences.

## Materials you will need for your group:



- Safety goggles
- An acid-base indicator such as bromothymol blue, diluted with water: 8 milliliters bromothymol blue ( $0.04 \%$ aqueous) to 1 liter of water
- Two clear $10-$ oz plastic cups (the tall ones)

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- Paper cups, 3-oz size (you'll only use one in the experiment, but keep a few extras at hand just in case)
- Masking tape
- Plain white paper
- Permanent marker
- Baking soda
- White vinegar
- Two Petri dishes to use as lids for the plastic cups
- Graduated cylinder or measuring spoons
- Gram scale or measuring spoons

Follow this procedure:


1. Put on your safety goggles.
2. Pour $11 / 2$ fluid ounces ( $40-50 \mathrm{~mL}$ ) of acid-base indicator solution into each of the two clear plastic cups.

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3. Add $1 / 2$ teaspoon ( 2 grams) of baking soda to the paper cup.
4. Tape the paper cup inside one of the clear plastic cups containing the indicator solution so that the top of the paper cup is about $1 / 2$ inch (roughly 1 centimeter) below the top of the plastic cup. Make sure the bottom of the paper cup is not touching the surface of the liquid in the plastic cup-you don't want the paper cut to get wet. The second plastic cup containing indicator solution will be your control.
5. Place both clear plastic cups onto a sheet of white paper and arrange another piece of white paper behind the cups as a backdrop (this makes it easier to see the change).
6. Carefully add 1 teaspoon (about $5-6 \mathrm{~mL}$ ) of white vinegar to the paper cup containing the baking soda (image below). Be very careful not to spill any vinegar into the indicator solution. Why? Immediately place a Petri dish over the top of each plastic cup. Why?

## To Do and Notice:

Position yourself so you are at eye level with the surface of the indicator solution and look closely.

- What do you observe?
- Where is the color change taking place?
- Explain your observations with a set of chemical equations?
- How can you connect this small-scale simulation of ocean acidification with the large-scale effects of climate change?
- Why are oceans so called "carbon sinks"?
- How is carbon regulation associated with temperature regulation on Earth?
- Why does human activity overburdens Earth's important thermostat?

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## What's Going On?

This activity illustrates how the diffusion of a gas into a liquid can cause ocean acidification. It also models part of the short-term carbon cycle-specifically the interaction between our atmosphere and the ocean's surface.

Mixing vinegar and baking soda together in the paper cup creates carbon dioxide gas $\left(\mathrm{CO}_{2}\right)$. The $\mathrm{CO}_{2}$ gas then diffuses into the liquid below. When $\mathrm{CO}_{2}$ gas diffuses into water, the following chemical reaction takes place and results in carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ :

$$
\mathrm{CO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{CO}_{3}
$$

Carbonic acid dissociates into $\mathrm{H}^{+}$and $\mathrm{HCO}_{3}$. The increase in $\mathrm{H}^{+}$causes the solution to become more acidic.

Carbonic acid is a weak acid. Even so, the presence of this acid affects the pH of the solution. Thus, after a short time, the surface of the indicator solution changes color: from blue to yellow if you're using bromothymol blue or from purple to pale pink if you're using cabbage-juice indicator. This color change indicates a pH change caused by the diffusion of $\mathrm{CO}_{2}$ gas into the liquid.

Outside of your paper cup, on a much larger scale, atmospheric $\mathrm{CO}_{2}$ diffuses into the oceans. Oceans are the primary regulator of atmospheric $\mathrm{CO}_{2}$. Human activities such as burning fossil fuels and changes in land use have increased the amount of carbon dioxide $\left(\mathrm{CO}_{2}\right)$ in the atmosphere from 540 gigatons of carbon ( Gt C ) in pre-industrial times to 800 Gt C in 2015.

Current atmospheric $\mathrm{CO}_{2}$ levels are greater than they have been in 800,000 years, and as a result, the fast carbon cycle is no longer in balance. From 1860 to 2009, the oceans absorbed an additional 150 Gt C from the atmosphere.

The $\mathrm{CO}_{2}$ taken up by the oceans reduces oceanic pH through a series of chemical reactions. The first of these is the reaction you just observed: the creation of carbonic acid via the diffusion of $\mathrm{CO}_{2}$ gas into water.

In pre-industrial times, the pH of the oceans was close to 8.2. In 2005, it was approximately 8.1. While the pH of the ocean is still basic, it is more acidic than it used to be. Since the pH scale is logarithmic, this means that the oceans are $30 \%$ more acidic now than they were in pre-Industrial times.

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## Going Further

Diffusion goes both ways-from the atmosphere into a liquid and from a liquid into the atmosphere. This experiment shows passive diffusion: the $\mathrm{CO}_{2}$ gas diffuses into the liquid.

- What experiment might you try in order to show that diffusion also goes the other way-from a liquid back into the atmosphere?

In March 2015, the global monthly average of the atmospheric concentration of $\mathrm{CO}_{2}$ was around 400 parts per million (ppm), or $0.04 \%$. It is a small amount, but it is increasing by more than 2 ppm every year due to the combustion of fossil fuels such as oil, gasoline, natural gas, and coal, as well as land-use changes such as deforestation.

Increases in the concentration of atmospheric $\mathrm{CO}_{2}$ have led to increases in the concentration of $\mathrm{CO}_{2}$ and other carbon-containing molecules in seawater.
The $\mathrm{CO}_{2}$ added to seawater reacts with the water molecules to form carbonic acid in a process known as ocean acidification. The oceans are absorbing about $25 \%$ of the $\mathrm{CO}_{2}$ we release into the atmosphere each year. Additionally, as more $\mathrm{CO}_{2}$ gas enters the atmosphere, the atmosphere gets warmer, causing global temperatures to rise.

Ocean acidification is expected to impact ocean species to varying degrees. Photosynthetic algae and seagrasses may benefit from higher $\mathrm{CO}_{2}$ conditions in the ocean, as they require $\mathrm{CO}_{2}$ to live (just like plants on land). On the other hand, studies have shown that a more acidic ocean environment has a dramatic effect on some calcifying species including oysters, shellfish, clams, sea urchins, shallow water corals, deep sea corals, and calcareous plankton. When shelled organisms are at risk, the entire food web may also be at risk.

# Part C: Destruction of Sea Shells (Eggshells) through Climate Change induced Ocean Acidification 

https://www.sciencelearn.org.nz/resources/159-ocean-acidification-and-eggshells

## Activity idea

In this activity, students observe how chicken eggs can be used to simulate the potential effects of increasing ocean acidity on marine animals with calcium carbonate shells or skeletons, for example, bryozoans, mussels and corals.

By the end of this activity, students should be able to:

- understand about ocean acidification and the possible impacts on shelled marine animals
- conduct an experiment that tests the effects of solutions of varying pH on eggshells


## Introduction/background

There is scientific evidence that suggests that the pH in our oceans is decreasing and therefore the oceans are becoming more acidic. This could have significant impacts on life in the sea.

For example, many marine species rely on calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$ to build a shell or skeleton. One of the effects of increasing acidity is a reduction in the availability of carbonate. This means that any animal that produces a calcium carbonate shell or skeleton will find it much more difficult to do so. Organisms could grow more slowly; their shells could become thinner or they might dispense with shells altogether.

A typical chicken eggshell consists of about 94-97\% calcium carbonate, so this experiment uses chicken eggs to simulate the potential effects of acidity on marine animals. As with shelled marine animals, eggshells vary between different species and vulnerability to acidity will vary with shape, thickness, structure and so on.

## pH and ocean acidification

pH is a measure of the acidity or alkalinity of a solution. Pure water is said to be neutral. The pH of seawater is about 8 but this varies slightly throughout the world.

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The world's oceans currently absorb as much as one-third of all $\mathrm{CO}_{2}$ emissions in our atmosphere. This causes the pH to decrease, resulting in the ocean becoming more acidic.

This could have significant impacts on life in the sea. For example, many marine species rely on calcium carbonate to build a shell or skeleton. One of the effects of increasing acidity is a reduction in the availability of carbonate. This means that any animal that produces a calcium carbonate shell or skeleton will find it much more difficult to do so. Organisms could grow more slowly; their shells could become thinner or they might dispense with shells altogether. It is difficult to predict the overall impact on the marine ecosystem, but many scientists fear that ocean acidification has the potential to decrease marine biodiversity on a very large scale.

## Links to New Zealand research

Abby Smith is a biogeochemist at the University of Otago. Part of Abby's research involves working on different bryozoan species and investigating how they respond when they are placed in solutions with different pH levels. The results have shown that a decrease in pH affects the skeletons of bryozoan species differently, depending on what they are made of and the shapes formed by their colonies. These results mean that some species of bryozoans have the potential to act as 'canaries in the coal mine' and provide early warning signs for areas that are at greatest risk from ocean acidification.

## Materials you will need for your group:

- 3 eggs
- 3 beakers or clear glass jars with lids to avoid spills (container should have at least 300 ml capacity)
- 250 ml tap water
- 50 ml vinegar
- 50 ml household ammonia
- pH Meter to adjust the pH of your solutions

Note: The amount of liquid required may vary according to the size of container used.

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## What to do:

1. As a class, watch the video clip Ocean acidification.
2. As a class, make a list of all the marine animals you can think of that have shells or skeletons made of calcium carbonate
3. Discuss the concept of pH and how this links to the oceans and life in the sea.
4. Set up and label 3 beakers:

- Acidic solution: 100 ml tap water and 50 ml vinegar
- Basic solution: 100 ml tap water and 50 ml household ammonia
- Neutral solution: 150 ml tap water

5. Place 1 egg into each beaker (make sure the eggs are all the same size and from the same carton). Have students record any observations.
6. Leave the beakers in a cool area for 24 hours. Have students observe each beaker again and record any changes.
7. Repeat for up to 4 cycles.
8. Lift the eggs carefully out of the solutions. Invite the students to carefully touch the eggs. Have students record any differences:

- After approximately 72 hours, the eggs in the acidic solution will no longer have a shell. This is because the acetic acid in the vinegar dissolves calcium carbonate. When the acid reacts with the calcium carbonate, carbon dioxide is released, which causes the bubbles the students may have observed.


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## Discussion questions:

- What did you observe with the 3 different solutions?
- What did the acidic solution represent?
- How do you think ocean acidification might affect marine animals with shells? What about those with skeletons?
- How do you think ocean acidification might affect the marine food web?
- Is there anything we can do to reduce ocean acidification?


## Extension ideas:

Students could experiment with seashells or with different vinegar concentrations.

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## Part D: Growing Sea Shells with Ocean Water at different pH

In this laboratory activity you will attempt to produce 1.00 g of calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$, which is the main component of the exoskeleton of sea shells and corals. You will prepare aqueous solutions of calcium chloride and sodium carbonate, which are the most dominant ions in ocean water. These solutions will be prepared from 2.01 g of calcium chloride and 1.06 g of sodium carbonate, two salts to be dissolved in water. Depending on the pH of the solution you will obtain more or less precipitated solid $\mathrm{CaCO}_{3}$.

## Materials you will need for your group:

- 3 beakers
- 100 mL graduated cylinder
- rubber policeman
- funnel
- filter paper
- squeeze bottle
- vinegar (5\%)
- household ammonia (5\%)


## Follow this procedure:

1. Put on your safety goggles.
2. Measure the pH of the provided water; it should read $\mathrm{pH} \sim 7$.
3. Obtain two clean beakers.
4. Obtain 2.01 g of calcium chloride and 1.06 g sodium carbonate at the weigh stations. You do not need exactly those amounts. Enter the exact masses you measured into your data table.
5. Add the calcium chloride to one beaker. Add enough water $(50-75 \mathrm{~mL})$ to dissolve the calcium chloride. Stirring will aid the dissolution process. Try to use a small amount of water so your filtration does not take too long.

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6. Add the sodium carbonate to the other beaker. Add enough water ( $50-75 \mathrm{~mL}$ ) to dissolve the sodium carbonate. Stirring will aid the dissolution process. Try to use a small amount of water so your filtration does not take too long.
7. Pour the calcium chloride solution into the beaker containing the sodium carbonate solution. Record your observations.
8. While waiting for the solid to settle, find the mass of a piece of filter paper. Record the mass in your data table.
9. Set up a funnel, filter paper, and Erlenmeyer flask. Wet the filter paper with a small amount of water.
10. Pour the contents of the beaker slowly into the funnel. Be careful as you pour, so none of the solid flows out of the filter paper or funnel. Use the bottle to remove as much of the solid from the beaker as possible ('lll show you how to do this at the start).
11. Once all of the solid is on the filter paper and the liquid has all drained through into the beaker, carefully remove the filter paper from the funnel without opening it up and set put it in the drawer for your class. You will obtain your final mass reading at the start of your next class (The solid needs to be dried)
12. Repeat the same steps as you did for pH 7 for $\mathrm{pH} 6.5 ; 7.5$ and 8.0 in order to simulate different ocean acidity levels. Adjust the pH values with the provided vinegar and household solutions.

Possible extension: Conduct titrations with burets and other analytic lab equipment for more accuracy

## Calculations:

1. Write the balanced chemical equation for the experiment.
2. Calculate the amount in $g$ of sodium carbonate to be used in order to obtain 2.00 g of $\mathrm{CaCO}_{3}$.
3. Calculate the amount in $g$ of calcium chloride to be used in order to obtain 2.00 g of $\mathrm{CaCO}_{3}$.
4. Given the initial recorded amounts as specified in the introduction calculate the theoretical yield and compare to the weighed yields at different pH values.

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## Discussion questions

- What is your percent error?
- What are potential error sources?
- What conclusions can you draw from your results about the effect of pH on calcium carbonate formation?
- Why is experimental accuracy so important to draw the correct scientific conclusions?



## Reference and further Reading:

NOAA Satellite and Information Services - Coral Reef Watch
https://coralreefwatch.noaa.gov/satellite/oa/description/oaps intro oa and reef.php
Science in service to the planet we call home
http://www.noaa.gov/

