



Vanishing Shells

Effects of Ocean Acidification on marine life

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Field-tested with: 11th grade students in the Chemistry course, BATA Academy, Watsonville High School, Watsonville, CA (2011-2012)

Concepts: pH, global warming, ocean acidification, human effects on ecosystems and populations, shell formation.

Skills: measure pH, apply science to investigate a real world problem, design and run an experiment to test an original question and hypothesis.

Module Type: Discussion and lab experiment

Duration: Two 2-h class sessions and two 45-minute class session

Key materials:

- Copies of ocean acidification news article
- News clip that goes with article
- pH strips or indicators
- Mussel and oyster shells
- Sea water
- White vinegar
- Timers
- Digital scales
- Rulers
- Beakers
- Pre and post lab questions

Science Education Standards:

National: Science As Inquiry; Science and Technology; Science in Personal and Social Perspectives

California: Chemistry: 3. Conservation of Matter and Stoichiometry, 5. Acids and Bases, 8. Reaction Rates; Biology-Life Sciences: 6. Ecology (ecosystem changes); Investigation and Experimentation

Overview:

This project is an opportunity for students to learn how increased carbon dioxide in the atmosphere decreases the ocean's pH and negatively affects shelled marine organisms. Specifically, students will learn:

- How to measure the pH of a solution.
- How fossil fuel combustion by humans increases carbon dioxide in the atmosphere and how that carbon dioxide is entering and changing the chemistry of the oceans.
- How an increase in carbon dioxide in oceans decreases ocean pH, causing ocean acidification.
- How ocean acidification reduces the calcium carbonate available to organisms that use it to create their shells, causing a decrease in shell thickness and strength.
- How to investigate the effect of ocean acidification on shelled organisms by designing and running an experiment to answer an original question and hypothesis.

Background for Teachers

Ocean acidification: Causes and Effects

Ocean acidification is a current and real environmental problem. Every day human activities such as driving and cooking require the combustion of fossil fuels, which increase the amount of carbon dioxide (CO_2) in the atmosphere. The atmosphere and ocean exchange gases through diffusion. Thus, more CO_2 in the atmosphere means more CO_2 in the ocean. Once in the ocean, CO_2 reacts with water in a way that both increases the acidity of the ocean and uses up important ocean carbonate molecules (CO_3^{2-}) that are needed by organisms such as mussels and oysters to form shells. In addition the increased acidity of the ocean eats away at shells, causing them to deteriorate (ScienceBridge 2011). In this module, students will learn about and investigate this phenomenon through inquiry-based lab experiments.

Science Education Standards Addressed: This module focuses on ocean acidification and its effects on shelled organisms and addresses NSES standards A. Science As Inquiry (p.175-176); B. Physical Science (176-181); C. Life Science (p.181-187); F. Science in Personal and Social Perspectives (p.198-199), as well as the following SCSCPS content standards:

Biology-Life Sciences:

6. Ecology: Stability in an ecosystem is a balance between competing effects.
 - b.** Students know how to analyze changes in an ecosystem resulting from changes in climate, human activity, introduction of nonnative species, or changes in population size.

Chemistry:

3. Conservation of Matter and Stoichiometry: the conservation of atoms in chemical reactions leads to the principle of conservation of matter and the ability to calculate the mass of products and reactants. As a basis for understanding this concept:
 - a.** Students know how to describe chemical reactions by writing balanced equations.
5. Acids and Bases: acids, bases, and salts are three classes of compounds that form ions in water solutions. As a basis for understanding this concept:
 - a.** Students know the observable properties of acids, bases, and salt solutions.
 - b.** Students know acids are hydrogen-ion-donating and bases are hydrogen-ion-accepting substances.
 - d.** Students know how to use the pH scale to characterize acid and base solutions.
8. Reaction Rates: chemical reaction rates depend on factors that influence the frequency of collision of reactant molecules. As a basis for understanding this concept:

- a. Students know the rate of reaction is the decrease in concentration of reactants or the increase in concentration of products with time. b. Students know how reaction rates depend on such factors as concentration, temperature, and pressure.

Investigation and Experimentation:

1. Scientific progress is made by asking meaningful questions and conducting careful investigations. As a basis for understanding this concept and addressing content in the other four strands, students should develop their own questions and perform investigations. Students will:

- a. Select and use appropriate tools and technology (such as computer-linked probes, spreadsheets, and graphing calculators) to perform tests, collect data, analyze relationships, and display data.
- b. Identify and communicate sources of unavoidable experimental error.
- c. Identify possible reasons for inconsistent results, such as sources of error or uncontrolled conditions.
- d. Formulate explanations by using logic and evidence.
- k. Recognize the cumulative nature of scientific evidence.
- l. Analyze situations and solve problems that require combining and applying concepts from more than one area of science.
- m. Investigate a science-based societal issue by researching the literature, analyzing data, and communicating the findings. Examples of issues include irradiation of food, cloning of animals by somatic cell nuclear transfer, choice of energy sources, and land and water use decisions in California.

NSES (<http://www.nap.edu/catalog/4962.html>)

SCSCPS (<http://www.cde.ca.gov/be/st/ss/documents/sciencetnd.pdf>);

The Chemistry of Ocean Acidification

The ocean is made up of many salts and dissolved gases, including oxygen and carbon dioxide from the air, that help maintain a constant **pH** in which marine organisms live. pH is a measurement of the amount of **hydrogen ions (H⁺)** in a solution; the more H⁺ in the water, the more **acidic** it is and the lower the pH (Fig. 1). Drinking water is around a pH of 7, so that means it has a more H⁺ in it than seawater, which has a pH of around 8 (Nybakken 2001). Ocean organisms have adaptations that allow them to breathe, move, and grow in the salty, basic seawater. They depend on the near constant level of salinity and pH in the ocean (Nybakken 2001).

Since the industrial revolution, however, the ocean's pH has been decreasing in a phenomenon known as **ocean acidification**. Ocean acidification is the decrease in the pH of seawater that results from the ocean absorbing the increasing load of carbon dioxide in the air. Carbon dioxide (CO₂) comes from many sources, including volcanoes and respiration, but human activities that burn fossil fuels now contribute to 75% of the CO₂ in the atmosphere and about 40% of that CO₂ goes into the oceans (IPCC, 2007).

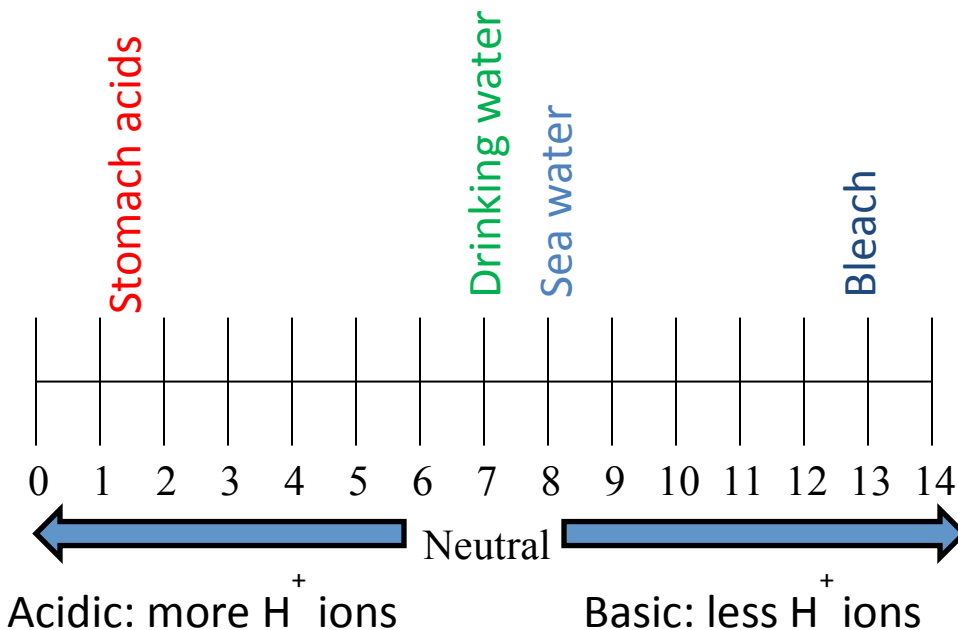


Figure 1. pH scale.

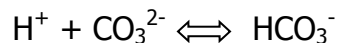
Once in the ocean, CO₂ combines with water to form carbonic acid (H₂CO₃) which subsequently gets broken down into bicarbonate (HCO₃⁻) plus a free hydrogen ion (H⁺), increasing the acidity of the ocean:

Equation #1



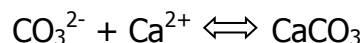
Some of those free hydrogen ions (H⁺) combine with free **carbonate** (CO₃²⁻) normally found in seawater to form more bicarbonate (HCO₃⁻):

Equation #2



This chemical reaction uses up important ocean carbonate (CO₃²⁻) molecules needed by some organisms, such as mussels and oysters, to form shells. In addition, the increased acidity of the ocean caused by the free hydrogen ions (H⁺), causes shells to deteriorate, or become thin and easily broken. Shells are formed by marine organisms taking up carbonate and calcium in seawater to form calcium carbonate, or the tough cement-like layer we know as a shell:

Equation #3



When the availability of carbonate (CO_3^{2-}) in the ocean is reduced because of ocean acidification (Equation #2), that means less is available to marine organisms to form shells! On top of that, when the overall **concentration** of carbonate (CO_3^{2-}) is reduced in the ocean, Equation #3 will reverse itself to maintain an equilibrium of carbonate (CO_3^{2-}) in the ocean, causing the shells to actually dissolve! This is a serious problem for our marine ecosystems, including shell-building coral reefs (Hardt and Safina 2008). Coral reefs are like the tropical rain forests of the oceans, meaning they are homes to thousands of species. Ocean acidification is also a huge problem for the multi-billion dollar mussel, clam, and oyster business, as you will read in the article "Ocean Acidification Reaches Northwest Hatcheries" (Bonfils 2010)

<http://abcnews.go.com/GMA/Eco/ocean-acidification-hits-northwest-oyster-farms/story?id=10425738>; and watch the video associated with it at: <http://abcnews.go.com/GMA/video/ocean-acid-10445789>

A local oyster fisherman and businessman, Bill the Oyster Man (billtheoysterman.com) needs help determining how ocean acidification affects the strength and appearance of his mussels and oysters. He needs your help to determine not only how acidity affects his shellfish, but also how the acidity reacts with other characteristics of the shellfish (i.e., species and size) as well as other methods of storing them (i.e., temperature). Your job is to investigate the different effects of acidity on one or both of these species of shellfish- what effects do you think are important for Bill? What comparisons can you make with the shellfish and storage methods?

Common Student Misconceptions:

Make sure students understand that putting the shells in vinegar is not equivalent to the process of ocean acidification and that it is just a sped up simulation of what happens to shells during ocean acidification. Similarly, remind students that the vinegar has a very low pH and that the ocean, even though it is becoming more acidic with increased carbon dioxide, is still basic overall. Also, while this module is meant for a chemistry class, the biology of the shelled organisms is equally important to the topic of ocean acidification. Thus, it is good to remind students that these shelled organisms are adapted to function biologically at a narrow pH range.

Project Description

Materials:

- Copies of ocean acidification news article: <http://abcnews.go.com/GMA/Eco/ocean-acidification-hits-northwest-oyster-farms/story?id=10425738>
- News clip that goes with article: <http://abcnews.go.com/GMA/video/ocean-acid-10445789>
- pH strips or indicators

- Solutions on which to measure pH: bleach, water, sea water, soda, coffee.
- Video of volcanic gas bubbles escaping near Ischia Island, Italy
- 2 gallons of sea water (or aquarium salt dissolved in water)
- Straws
- Parafilm wax covers
- Pipettes (if using pH universal indicator)
- Mussel and oyster shells
- White vinegar
- Timers
- Digital scales
- Rulers
- Beakers
- Hot plate
- Ice bath
- Pre and post lab questions

Preparation:

- Purchase or obtain mussel and oyster shells. Bay mussels (***Mytilus galloprovincialis***) or the Pacific oyster (***Crassostrea gigas***) are examples.
- Print copies of the news article, pre lab questions, and post lab questions
- For day 2, set up blowing into seawater demonstration, by putting seawater and pH indicator into a beaker, cover it with parafilm.
- Set out all materials before class on day of lab
- Depending on the level or status of your class, prepare lectures or discussion points about pH, chemical equations, and concentrations (i.e., saturated, unsaturated).

Timeline:

Day 1 (minimum day 45 minutes)

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|------------|---|
| 10 minutes | Lecture and discuss pH |
| 20 minutes | Students practice measuring pH on different solutions |
| 5 minutes | Watch video of gas bubbles escaping near Ischia Island, Italy |
| 10 minutes | Discuss what is going on in the video |

Day 2 (block period 110 minutes)

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|------------|---|
| 15 minutes | Perform the blowing into seawater demonstration and discuss questions about demonstration |
| 30 minutes | Lecture and discuss pH, the chemistry and effects of ocean acidification, and shell formation |
| 10 minutes | Discuss the importance of shelled organisms and coral reefs to ecosystems and fisheries |
| 15 minutes | Distribute and read news article |

15 minutes Watch related news movie and discuss
30 minutes Give students prompt for inquiry, break them up into groups, and have them brainstorm and come up with a question to answer in the next period's lab

Day 3 (block period 110 minutes)

10 minutes Briefly review material covered in Day 2
10 minutes Students answer pre lab questions and formulate a hypothesis
10 minutes Students get back in their groups and review their lab questions
10 minutes Students get their shells and write down observations
60 minutes Students perform lab and while waiting for the shells to sit in acid (at least 30 minutes) answer post lab questions and work on lab report
10 minutes Teachers make sure students have results recorded or allow students to continue their experiments until next class period.

Day 4 (minimum day 45 minutes)

10 minutes Students get into groups and briefly summarize results
15 minutes Students report their results to the class and findings are discussed
20 minutes Students work on their lab report, which is due the next class period

Procedure:

Day 1 (minimum day 45 minutes)

- Before class starts, download the video showing gas bubbles from the volcano near Ischia Island, Italy and how the CO₂ gas affects shelled organisms there. The video can be found at Nature.com at <http://www.nature.com/nature/journal/v454/n7200/supinfo/nature07051.html> Also before class starts, put out the items for pH testing in small containers on each table (or group the students and have one container of each solution for each group).
- Briefly talk about what pH is (see "Background for Teachers: The Chemistry of Ocean Acidification" above for key points or use your own lecture).
- Pass out the pH indicator strips, explain how they work, and allow students to practice measuring pH on the different substances- including seawater.
- Have the students watch the Ischia Island video and ask them what they think it is showing. Watch it again and tell them to pay attention to the state of the organisms shown at the end of the video.
- Have a discussion about the video: tell them this video is showing Carbon Dioxide bubbling into the ocean from volcanic vents under the sea. Tell them the scientist is studying how the CO₂ affects the ocean and the shelled organisms and they are going to investigate this in the next few class periods.

Day 2 (block period 110 minutes)

- Before class, set up the “blowing in sea water” demonstration by putting seawater in a beaker, add the pH indicator, cover it with parafilm, and poke a straw through the parafilm.
- Perform the blowing into seawater demonstration and discuss the chemical reaction and questions about demonstration (see “Blowing in sea water demo discussion questions” below).
- Lecture and discuss pH, the chemistry and effects of ocean acidification, and shell formation (see “Background for Teachers: The Chemistry of Ocean Acidification” above for key points or use your own lecture).
- Discuss the importance of shelled organisms and coral reefs to ecosystems and fisheries. Give a brief lecture on how seashells are formed by shellfish, including oysters and mussels, clams, scallops (bivalves), all of which are commercially important types of shellfish and all being raised commercially by aquaculture.
- Provide, read and discuss the news article on the effects of ocean acidification on the pH of seawater and how upwelling of this seawater has negatively affected the formation of larval oysters and the subsequent impact on the aquaculture industry on the west coast of North America.
- Watch related news movie and discuss. Here are some potential discussion questions to get them thinking about the issue and the up-coming lab:

Discussion Questions:

1. How do you feel about the reading/movie?
2. What are possible sources of increasing acids in seawater?

Add to the student list of sources of acids in seawater. Stress the effects of combustion of fossil fuels and respiration of breathing organisms.

3. How are solid seashells formed from seawater?
 4. What is the chemical equation for the formation of seashells?
 5. How do acids affect seashell formation?
 6. How do we measure the amount of acid in seawater?
- Finally, give students the prompt for inquiry (see “Starting point for inquiry”) and break them up into groups of 3-4 students. Give students time to brainstorm questions and ways to help out “Bill the Oyster Man”. See “Help with Question generation” section for assistance in this matter.
 - Make sure all students groups and come up with a testable question to answer in the next period’s lab.
 - Before the next class period, make sure that you have all the materials necessary for each group to test their specific question.

Here are the essential questions students will generally be forming their hypotheses around:

• **How does ocean acidification affect shellfish?**

• **How do different environmental factors affect how ocean acidification affects shellfish?**

• **Does ocean acidification affect different shellfish in different ways?**

• **Do environmental factors change the way ocean acidification affects species differently?**

Students brainstorm possible environmental factors that may affect the influence of pH on the shells of shellfish. These factors might include:

- The amount of acid in the seawater
 - The size/mass of the shells
 - The surface area of the shells
 - The top shell of the shellfish (oysters) compared to the bottom shell of the shellfish
 - The temperature of the seawater
 - Other factors
- Students choose a factor to investigate. The students will use bay mussels (*Mytilus galloprovincialis*) or the Pacific oyster (*Crassostrea gigas*) for their experiments.
 - Students will brainstorm a set of procedures to do their experiment. Their procedures will be reviewed by the teachers and approved or returned for further modifications.
 - Generally, to answer the above essential questions, students will should come up with a procedure that requires them to keep the shells in sea water (as a control) and sea water + acid for a period of time- at least 30 minutes is required- to see differences in the control and acid affected shell. Other students will do this comparison but on ice or in heated water to test the affect of temperature. Other questions may relate to the specific shell characteristics, so students will need to spend some time observing and measuring their shells beforehand.

Day 3 (block period 110 minutes)

- Before class starts, set out all necessary lab materials.
- Briefly review materials covered in Day 2 and have students get back in their groups and to review both their lab questions and their procedures.
- Hand out pre-lab questions (see “pre-lab questions” below) and give students 10 minutes to answer the questions and formulate a hypothesis (if they haven’t already done so in the previous class period). After 10 minutes, go over the pre-lab questions as a class.
- Before students begin their lab, make sure the students take time to measure and mass their shells pre-treatment. Thus, before students pick up the shells, remind them to first observe the shells for 10 minutes, recording all of their observations.
- After observations, allow the student to begin testing their questions. Encourage them to nominate one group member to collect all the materials they need.
- While students are waiting for their experiments to carry out (i.e. waiting the minimum 30 minutes for the shells to sit in the water), have students answer the post-lab questions (see “post-lab questions” below). They can also use this time to start working on their lab reports.
- In the last 10 minutes of class, make sure students have recorded their results.
- In some cases, students may want to allow the shell to sit in the water for longer than 30 minutes and so you may allow them to leave their shells, and thus results collection, for the next class period.

Day 4 (minimum day 45 minutes)

- Have students get back into their groups and record and/or review their results.
- Once all student groups have results, have them report their results to the class. Summarize the results as a class and discuss the findings in terms of the effects of acidification on shelled marine species.
- Any remaining time allow students to work on their lab reports, which are due in the next class period. Meet with groups to discuss their analysis and teamwork.
- Each student turns in a lab report including:
 - Lab protocol
 - Control trial data
 - Lab trial data
 - Analysis questions
 - Evaluation of lab members

Starting Point For Inquiry:

First have students read the article “Ocean Acidification Reaches Northwest Hatcheries” (Bonfils 2010) <http://abcnews.go.com/GMA/Eco/ocean-acidification-hits-northwest-oyster-farms/story?id=10425738>; and watch the video associated with it at: <http://abcnews.go.com/GMA/video/ocean-acid-10445789>.

Second, give them the inquiry prompt: a local oyster fisherman and businessman, Bill the Oyster Man (billtheoysterman.com) needs help determining how ocean acidification affects the strength and appearance of his mussels and oysters. He needs your help to determine not only how acidity affects his shellfish, but also how the acidity reacts with other characteristics of the shellfish (i.e., species and size) as well as other methods of storing them (i.e., temperature). Your job is to investigate the different effects of acidity on one or both of these species of shellfish- what effects do you think are important for Bill? What comparisons can you make with the shellfish and storage methods?

Third, have a discussion about the possible questions students could answer and how they can help Bill with different experiments. Show them the materials to get them thinking further about possibilities.

Fourth, break students up into groups of 3-4 and allow them to brainstorm as a group what question they want to investigate.

Help with Question Generation:

Students should come up with questions on their own, but may need some hints, as included in the "Starting point for inquiry" above, such as comparing "species" and "sizes" of the shellfish or how acid affects them at different "temperatures". Students may come up with entirely novel ideas and may require additional materials, if available. If students are struggling to come up with a question, keep reminding them of the real world context and how Bill really is a business man and wants his shellfish to look great and feel strong when he sells them. In this way, students could test the effect of acidity on the appearance of the shells, even draw them for comparison. In every case, however, students will need to compare shellfish before being placed in acid and after, or a control (no acid) and acid comparison. Once the question is determined, students will mostly likely need assistance in developing a datasheet, or a table to record their data whether they are size, weight, or appearance of the shellfish.

Presenting Final Results and Assessment Methods:

- Each student group must present their results to the class in the form of a verbal explanation and/or drawing any graphs on the board.
- Each student turns in a lab report including:
 - Lab protocol
 - Control trial data
 - Lab trial data
 - Analysis questions
 - Evaluation of lab members
- Lab reports are graded and teachers meet with students to discuss their lab procedures, execution, analysis and work as a team.

Appendices

The following discussion, pre-lab, and post-lab questions were adapted from the ScienceBridge Ocean Acidification Teacher Guide (2011). Worksheets are downloadable from the module page.

Blowing in sea water demo discussion questions:

1. What gas am I blowing into the water?

Carbon dioxide (CO₂)

2. What happens to the gas when I blow it into the water?

Some gas comes back out as bubbles and some is dissolved by the water

3. What is the reaction that is happening?



4. How does carbonic acid (H₂CO₃) affect the water?

It breaks down and adds more hydrogen ions to the water, making it more acidic

5. How are we measuring change in the water while I blow into it?

The pH indicator is changing color

6. What does measuring the pH of the water tell us?

Whether is it becoming more acidic or basic

See attached worksheets:

Pre-lab questions

1. How do organisms make their shells? What are shells made of? Write out both the chemical formula and the material.

2. What do you expect to happen to the shell in an acidic solution such as vinegar?

3. What are sources of carbon dioxide and which of these sources are most likely to

affect ocean pH?

4. Hypothesis

Post-lab questions

1. When you immersed the shells in vinegar, how did you know that a reaction was happening?

2. Write down the chemical reaction you just observed. The chemical formula for acetic acid (vinegar) is $C_2H_4O_2$.

3. What type of gas is being produced by this reaction?

4. How is this reaction similar/different from the reaction during the bubbles protocol?

5. How did observing the shells in vinegar relate to how animals are affected by a lower pH of ocean water?

6. How would shelled organisms be affected by a lower pH of ocean water?

7. What are the primary functions of shells for these animals?

8. Does it cost the animal energy to rebuild or repair their shell?

9. Conclusion / summary (revisit hypothesis)

Pre-lab answer key

1. How do organisms make their shells? What are shells made of? Write out both the chemical formula and the material.

Shells are made when the organism takes in chemicals it needs from the water surrounding it, alters the chemistry internally, then secretes the hard shell. Shells can be made of calcium carbonate (CaCO₃).

2. What do you expect to happen to the shell in an acidic solution such as vinegar?

Answers may vary here, but many students may put melt or dissolve.

3. What are sources of carbon dioxide and which of these sources are most likely to affect ocean pH?

Sources of carbon dioxide include volcanoes, methane breaking down into CO₂ (from cows, tundra, etc.), human emissions of green- house gases, exhaling by plants and animals, exchange with the ocean, and the breakdown of plant

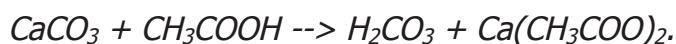
matter, among others. Likely sources to affect pH need to be in great enough concentrations to alter the water. On a local scale, volcanoes are the most likely. On a global scale, there must be a process which is not naturally balanced to reduce the pH, which includes human emissions of greenhouse gases.

Post-lab answer key

1. When you immersed the shells in vinegar, how did you know that a reaction was happening?

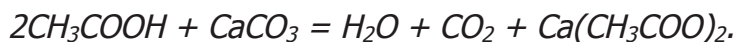
Bubbles formed on the outside of the shell and were visible in the water. The pH of the water began to change to a more basic pH.

2. Write down the chemical reaction you just observed. The chemical formula for acetic acid (vinegar) is CH_3COOH .



Step two of this equation involves the breakdown of carbonic acid into CO_2 and water: $\text{H}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_2$.

The overall reaction is the sum of these two reactions:



3. What type of gas is being produced by this reaction and what does it do to pH?

Carbon dioxide CO_2 and it lowers the pH of the water.

4. How is this reaction similar/different from the reaction during the bubbles protocol?

This is the reverse of the bubbles reaction in which CO_2 and water mix to create carbonic acid. Through this reaction CO_2 is released, lowering the pH.

5. How did observing the shells in vinegar relate to how animals are affected by a lower pH of ocean water?

Animals in a lower pH ocean are exposed to that pH for longer periods of time, we are testing what a shorter period of time does to an animal. The vinegar was far more acidic than the ocean will be, so this is not a direct observation of what would happen in the ocean. However, this does demonstrate the process by which shells are dissolved.

6. How would shelled organisms be affected by a lower pH of ocean water?

Shelled organisms would not be able to build their shells as quickly, and their shells would be dissolved. This could leave them open to predation, kill their food, or kill them outright by becoming too acidic to live in.

7. What are the primary functions of shells for these animals?

Shells provide a hard body for the organism, protecting it from predation. Shells can also act as a signal to a potential mate, protect an organism from the sun or dessication, and anchor and organism to a substrate.

8. Does it cost the animal energy to rebuild or repair their shell?

Yes. To survive, an organism needs to be able to maintain its shell, and doing so uses energy. The organism must bring in the proper materials to make its shell, convert those to a useable form, and then resecret this material as a shell.

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