Shell Shifts

Discover how ocean acidification can give some sea critters shell shock.

Materials

assorted sea shells
vinegar
calcium chloride ($CaCl_2$, sold as “Damp Rid” in stores)
baking soda ($NaHCO_3$, sodium bicarbonate)
0.25 M sodium hydroxide (NaOH, sold as lye in stores)
water
cups
spoons
(optional) pH indicator - cabbage juice, bromothymol blue, phenol red, etc

To do and notice

1. Place a shell in a cup and cover it with vinegar. What do you notice?
2. Make a sodium bicarbonate solution by adding one spoonful of baking soda to one cup of water. Make a separate calcium chloride solution by adding one spoonful of Damp Rid to one cup of water. Stir each solution well. How would you describe the solutions?
3. In a new cup, pour equivalent amounts of the $NaHCO_3$ and $CaCl_2$ solutions. Mix well. What do you notice when the two solutions mix? How has the mixture changed?
4. Add small amounts of vinegar until you notice a change. Keep mixing the sample throughout.
5. Add small amounts of the NaOH solution until you notice a change. Keep mixing the sample throughout.
6. (optional) Add a small amount of pH indicator in step 3 to keep track of the pH throughout the experiment.

What’s going on?

The primary component of most seashells is calcium carbonate ($CaCO_3$). You may have noticed bubbles forming when you put a shell into vinegar. The bubbles are carbon dioxide that is created when $CaCO_3$ is exposed to an acid such as vinegar.

$$CaCO_3 + 2H^+ \Leftrightarrow Ca^{2+} + CO_2 + H_2O$$

Sodium bicarbonate and calcium chloride both dissolve pretty well in water.

$$NaHCO_3 \rightarrow Na^+ + HCO_3^-$$
$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$$

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The solutions you made with them should be relatively clear. In water, bicarbonate (HCO_3^-) is never by itself, but is present in equilibrium with other forms of dissolved inorganic carbon, carbonic acid (H_2CO_3) and carbonate (CO_3^{2-}).

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3^{2-} + 2H^+$$

When you mix them together, the carbonate ion (CO_3^{2-}) reacts with the Ca^{2+} ion to form calcium carbonate.

$$CO_3^{2-} + Ca^{2+} \Leftrightarrow CaCO_3$$

The mixture should turn cloudy since $CaCO_3$ is not very soluble in water and will form a precipitate. You just made bits of shells!

When you add vinegar to this mixture, the excess H^+ ions will dissolve the $CaCO_3$ particles, just like it did to your seashell, and the solution should turn clear. There should be tons of bubbles because the bicarbonate in solution will also react to from CO_2. Adding a base will shift the equilibrium back to solid $CaCO_3$, and you should see a cloudy precipitate. This shows how sensitive $CaCO_3$ is to the pH of its environment.

Going further

A wide variety of ocean organisms from shellfish and corals to certain kinds of algae contain calcium carbonate in their exoskeletons. Increasing levels of CO_2 in the atmosphere are creating an increase in levels of dissolved inorganic carbon and a decrease of the pH in the oceans, a phenomenon called ocean acidification. The carbon species you worked with in this activity are all in a dynamic equilibrium, with the bicarbonate form (HCO_3^-) representing over 90% of the dissolved inorganic carbon at ocean pH.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow CO_3^{2-} + 2H^+$$

The minerals in the ocean contain an large amounts of carbonate, so another reaction that occurs is:

$$CO_2 + H_2O + CO_3^{2-} \Leftrightarrow 2HCO_3^-$$

These two reactions show how increasing CO_2 can lower the pH and reduce the concentration of CO_3^{2-}. The lower concentration of carbonate reduces the amount available for calcifying organisms that span the food chain to use and drives the equilibrium to dissolve more $CaCO_3$ rocks in the ocean. The graph below shows the equilibrium ratios of different carbon species in seawater at a range of pH levels.

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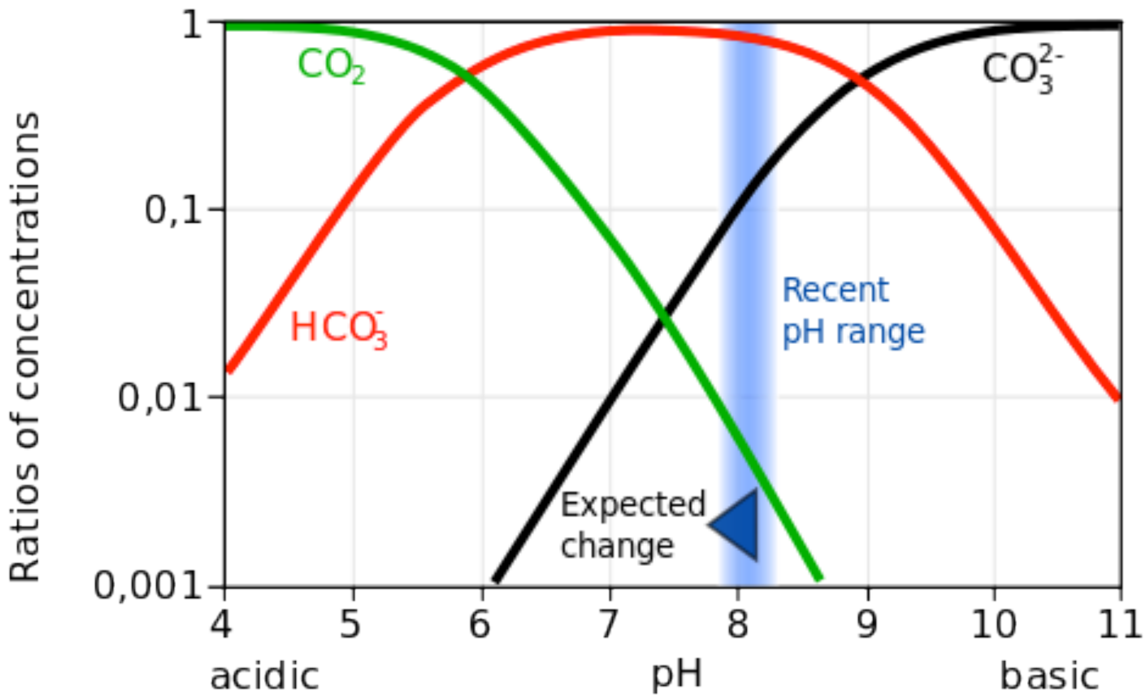

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