Student 1: Excellence

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The net reaction for the chemical process of ocean acidification is shown by the following equation:

$CO_{2\,(aq)} + H_2O_{(l)} + CO_3^{2-}{}_{(aq)} \rightarrow 2HCO_3^-{}_{(aq)}$

This reaction can be broken down into smaller, more specific reactions, allowing greater understanding into the issues and processes of ocean acidification, and therefore a better array of knowledge as to how its effects can be eliminated or reduced.

$CO_{2\,\mathbf{(g)}} \rightleftharpoons CO_{2\,\mathbf{(aq)}}$

The first reaction taking place is the absorption of the carbon dioxide in the atmosphere into the ocean waters. Of the world's carbon dioxide, approximately 93% is stored within the oceans inside algae, vegetation and coral, thus the ocean is named the world's largest 'carbon sink', and of the carbon dioxide released due to human activities over one third is absorbed into the oceans, though exact values vary depending on the source. In this reaction, the carbon dioxide is shifting from its natural gaseous state to an aqueous state, as it does during the absorption process of the carbon dioxide. This change occurs due to the natural strive for equal conditions of carbon dioxide between the atmosphere and oceans and is therefore an equilibrium reaction, sometimes requiring centuries or millennia to come into solubility equilibrium with the entire ocean.

$CO_{2\,\mathbf{(aq)}} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)}$

The second reaction taking place is the now aqueous carbon dioxide reacting with water in an equilibrium reaction to form carbonic acid. Now dissolved, the carbon dioxide (CO_2) rapidly reacts with water forming carbonic acid (H_2CO_3), as well as further acid-base and ionic solubility reactions. 1

$H_2CO_{3\,(aq)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+{}_{(aq)}$

The third reaction taking place is the dissociation of the carbonic acid into bicarbonate ions (HCO_3^-) and hydrogen ions (H^+). The hydrogen ions are acidic, which therefore directly contributes to the lowering of the ocean's pH, while the bicarbonate ions are basic. In this reaction, the equation favours the products, due to the continuing excess concentrations of hydrogen ions.

$H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons 2HCO_3^-{}_{(aq)}$

The next reaction taking place is the reacting of a number of the hydrogen ions produced in the previous reaction with basic carbonate ions (CO_3^{-2}) to form more basic bicarbonate ions. The carbonate ions are available for the hydrogen ions to react with as they naturally saturate saline water. As seen in a typical acid-base reaction, the acidic hydrogen donates as opposed to accepting, and in this specific reaction it's only the H^+ atom being donated to the basic carbonate ion. In this reaction, the equilibrium favours the product as the excess hydrogen ions react with the carbonate ions to form increased concentrations of product, bicarbonate ions (HCO_3^-).

$CaCO_{3\,(s)} + 2H^+{}_{(aq)} \rightarrow Ca^{2+}{}_{(aq)} + CO_{2\,(aq)} + H_2O_{(l)}$

Another reaction that may be of significance is the reaction between calcium carbonate and acidic hydrogen ions. The calcium carbonate reacts with the acidic hydrogen ions to produce carbon dioxide gas, as well as aqueous water and calcium ions.

For the last several hundred thousand years, the oceans have been kept at a relatively stable and slightly alkaline (≅8.2) state due to the carbonate buffer system. This is a series of reactions, in which dissolved carbon dioxide is converted to bicarbonate using carbonate as a buffer, therefore having kept the level of hydrogen ions, and therefore the pH, constant. The chemical reactions that form bicarbonate, carbonate and calcium carbonate are equilibrium reactions, as they can favour either the products or reactants depending on conditions such as increases or decreases of carbon dioxide, pressure and temperature. Under normal physical and biological conditions, the carbonate-bicarbonate ions act as a 'bank' that automatically takes up excess carbonic acid or other acids, or forms more carbonic acid if carbon dioxide is lost. This is the buffer system that maintains the normal pH of saline water at approximately 8.2 (a buffer 3 solution resists changes in pH when acid or alkali is added). Bicarbonate (HCO^{3-}) is the most important in maintaining this normal range, as its production leads to a further uptake of carbon dioxide. Thus, the carbonic acid/carbonate equilibrium determines the amount of free protons in the saline water, and by extension the pH value. Calcium (Ca^{2+}) is also an important element presence in saline water and this system, and is imperative for building strong coral skeletons, mollusc shells and algal support, alongside various other biological uses. As the calcium carbonate ($CaCO_3$) is removed from saline water by biological and chemical processes, more bicarbonate ions form from carbonate and more carbon dioxide is absorbed into the buffer system, so the pH remains fairly constant. In the ocean, carbon dioxide enters the system through water runoff from the land and through areas with high biological activity, where it then accumulates in the ocean depths before being released back into the atmosphere in areas where deep sea waters well upwards towards the surface (upwelling). The bicarbonate/carbonate buffer system equilibrates backwards and forwards, though the pH remains relatively constant.

If the amount of carbon dioxide in the atmosphere stabilises, eventually buffering/neutralising will return the pH to normal as demonstrated in the past, where periods of highly elevated carbon dioxide showed no evidence of ocean acidification as the rate of carbon increase was slower, thus allowing the oceans time to buffer and adapt. However, presently the rate of carbon increase is too rapid, and the pH is dropping too quickly, meaning the buffering will take hundreds, if not thousands of years, far too long for the oceans organisms affected now and indeed in the near future. The pH of the ocean fluctuates within limits as a result of natural processes; meaning ocean organisms are well adapted to survive the changes they normally experience. Therefore although some organisms may be able to adapt to more extreme changes, many will suffer and there are likely to be extinctions. A more acidic ocean won't destroy all marine life, but the rise in seawater acidity of 30% that has recently been recorded is already affecting organisms. The average pH of the surface waters is currently 8.1, approximately 0.1 pH unit less than the estimated pre-industrial value two hundred years prior. The present changes in the pH of the ocean's saline water has been shown to be having harmful effects on all manner of marine life, impacting processes vital to survival such as chemical communication, reproduction, and growth. 4

The building of skeletons/shells in marine creatures is particularly sensitive to acidity. One of the molecules that hydrogen ions (H^+) bond with is carbonate (CO_3^{-2}), a primary component of calcium carbonate ($CaCO_3$) shells. In order to make calcium carbonate, shell-building marine organisms such as corals and oysters combine calcium ions (Ca^{2+}) with carbonate (CO_3^{-2}) from surrounding saline water, producing carbon dioxide and water as by-products of the process.

Similarly to calcium ions, hydrogen ions tend to bond with carbonate, though they have a greater attraction to carbonate than calcium. When two hydrogens bond with carbonate, a bicarbonate ion ($2HCO^{3-}$) is formed. However, shell-building organisms cannot extract the carbonate ions they need from bicarbonate, thus preventing them from using that carbonate to grow new shells. It is in this way hydrogen essentially binds up the carbonate ions, making it harder for organisms like mussels and oysters to build their homes. 2 Even if the organisms manage to build skeletons in more acidic water, they need to spend more energy in order to do so, thus taking resources from other activities like reproduction. If there is an excess of hydrogen ions around them and not enough carbonate ions for them to bond with, the H^+ ions can even begin breaking existing calcium carbonate ($CaCO_3$) molecules apart, dissolving shells that already exist. Hydrogen ions also react with the carbonate ions in the ocean, removing it and thus under saturating the water. This causes the shells to dissolve back into carbonate ions in order to re saturate the oceans, re-establishing equilibrium:

$CaCO_{3\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{-2}{}_{(aq)}$. The dissolution is necessary as the carbonate ions are bonding to the hydrogen ions, and thus forming bicarbonate, not only removing the carbonate from the oceans but rendering it inaccessible to all manner of shell-building organisms who are unable to extract the carbonate they need from bicarbonate ions. This is just one example of how extra hydrogen ions, caused by dissolving carbon dioxide, may interfere within the ocean.