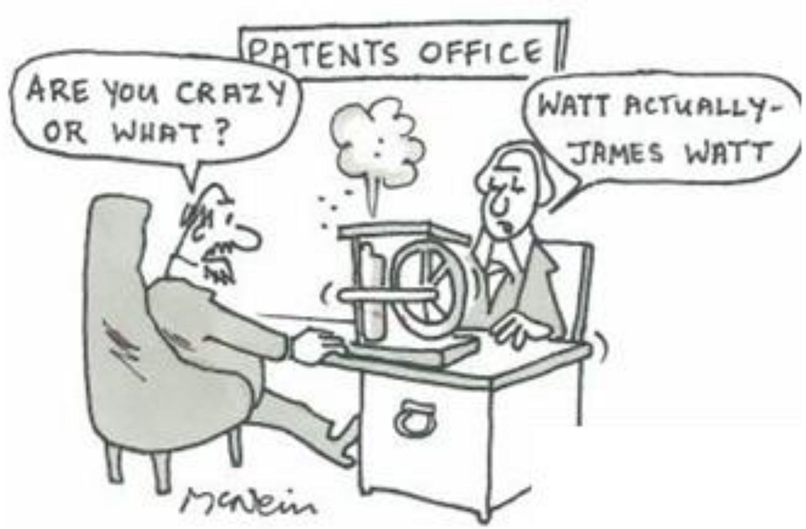
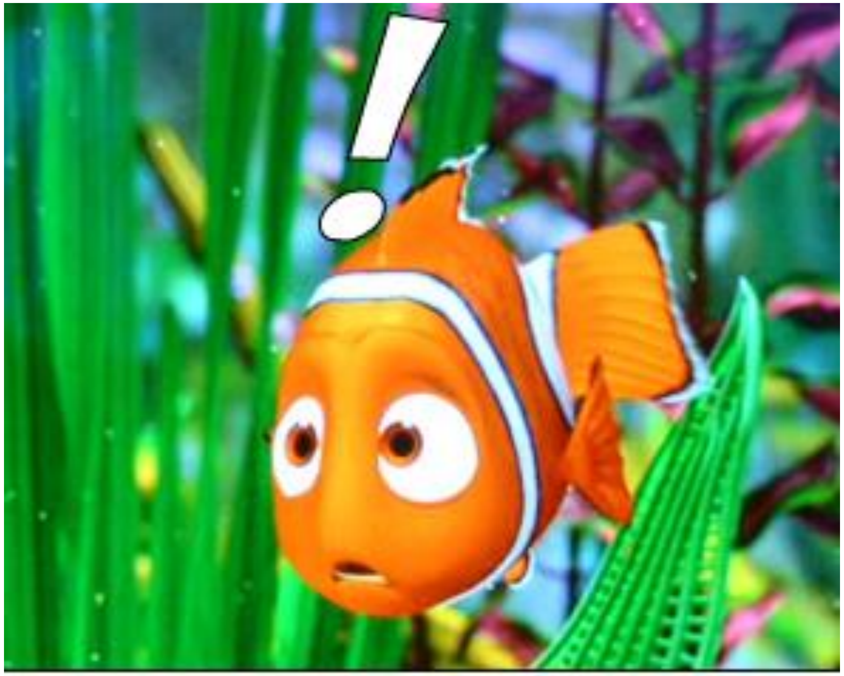


Ocean Chemistry



AND WHAT ABOUT NEMO HIMSELF, AND HIS FISHY PALS? HOW WILL OCEAN ACIDIFICATION AFFECT THEM?

Take a deep breath. It's possible that among the molecules of the CO_2 you inhaled some were emitted from burning the first tonne of coal in the first steam engine built by James Watt—the engines that powered the Industrial Revolution.

- https://fmss12ucheme.wordpress.com/2013/05/05/ocean-acidification-2/
- https://www.youtube.com/watch?v=gHdTso94Xt4

Introduction

The ocean is a carbon sink

1. A **carbon sink** is a natural or manmade reservoir that accumulates and stores some carbon-containing chemical compound for an indefinite period.

2. The ocean is the largest natural carbon sink on Earth.

Carbon dioxide in the ocean

1. Some marine organisms use carbon dioxide to live. Carbon dioxide is taken up by marine plants and algae during photosynthesis.

2. When carbon dioxide dissolves in seawater, most of it becomes bicarbonate ions and hydrogen ions. This increase in hydrogen ions is what decreases the pH. In addition, some of the hydrogen combines with carbonate to form more bicarbonate, decreasing the concentration of carbonate in seawater. Many marine organisms use carbonate, combined with calcium, to form their exoskeletons, shells or other structures (e.g. corals).

Introduction

- Almost all of the carbon in the atmosphere, the ocean, and the sediments is in its most oxidized form as CO_2 or carbonates, HCO_3^- and CO_3^{2-}, in solution or precipitates, largely $CaCO_3$.
- The interactions had been essentially in equilibrium for millennia before the Industrial Revolution. The sudden injection of CO_2 into this chemical system has upset the balance and we are now observing the effects of the disturbed annual to centennial interchanges noted in the figure.

Reactions going on in the ocean-atmosphere system.

- The solubility of CO_2 in seawater increases with the pressure of the gas and decreases as the temperature and salinity of the seawater increase. The dissolution equilibrium reaction is
- $CO_2(g) \Leftrightarrow CO_2(aq)$

- Once dissolved, the following reactions take place.
- $CO_{2(aq)} + H_2O_{(l)} \Leftrightarrow H_2CO_{3(aq)}$

This heterogeneous equilibrium reaction sees the dissolving of carbon dioxide in water to form carbonic acid.

This is a reversible reaction, and therefore the reaction will shift to reach a state of equilibrium where the rate of the forward reaction is equal to that of the reverse.

With Le Chatliers's principle in mind when looking at this specific reaction, we know that if more reactant is added (CO_2), that the reaction will shift to create more product (H_2CO_3).

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

- This acid-base equilibrium reaction sees the ionisation of carbonic acid into its hydrogen ions and bicarbonate anions. This is as well a reversible reaction and therefore the reaction continually works towards reaching equilibrium.
- As stated above, the increase in CO_2, according to Le Chatlier's Principle, will increase the amount of carbonic acid formed, and when more carbonic acid is formed, referring back to Le Chatlier's principle, we will see that the bicarbonate and hydrogen will become more abundant. **This increase in hydrogen ions over time increases the acidity of the ocean (decreases pH)**

$CaCO_3$ Sediments and shell formation Carbonate Equilibria

The concentration of carbonate ions in the oceans is limited by the solubility of calcium carbonate as follows:

$$Ca^{2+} + CO_3^{2-} = CaCO_3. \quad \text{Calcification} \quad (8)$$

Many marine organisms, however, utilize calcium and carbonate ions to form $CaCO_3$ skeletons, shells, scales and teeth, and they do so mainly on the surface of the ocean. As the organisms die, their shells and skeletons sink to a level where the temperature is low enough or the pressure high enough to make the water undersaturated with respect to $CaCO_3$. It is at that point they start to dissolve. The accumulation of undissolved $CaCO_3$ in the sediments over millions of years makes these sediments a major sink of carbon over geological time. Since calcium and carbon are always in abundant supply, they are not considered nutrients.

A decrease in pH (increase in H^+ concentration) affects the position of the following equilibrium with carbonate ions:

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

As the H^+ concentration increases, the equilibrium shifts to the right, consuming carbonate ions (CO_3^{2-}). This disturbs the following equilibrium with calcium ions, carbonate ions and solid calcium carbonate. A decrease in CO_3^{2-} drives the reaction to the left, causing calcium carbonate to dissolve:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$$

This makes it more difficult for marine organisms to produce and maintain their skeletons.

Ocean Equilibrium

There are interrelated equilibria in sea water that involve carbon dioxide and the hydrogencarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) ions.

These equilibria are illustrated in Figure 3.2.1.

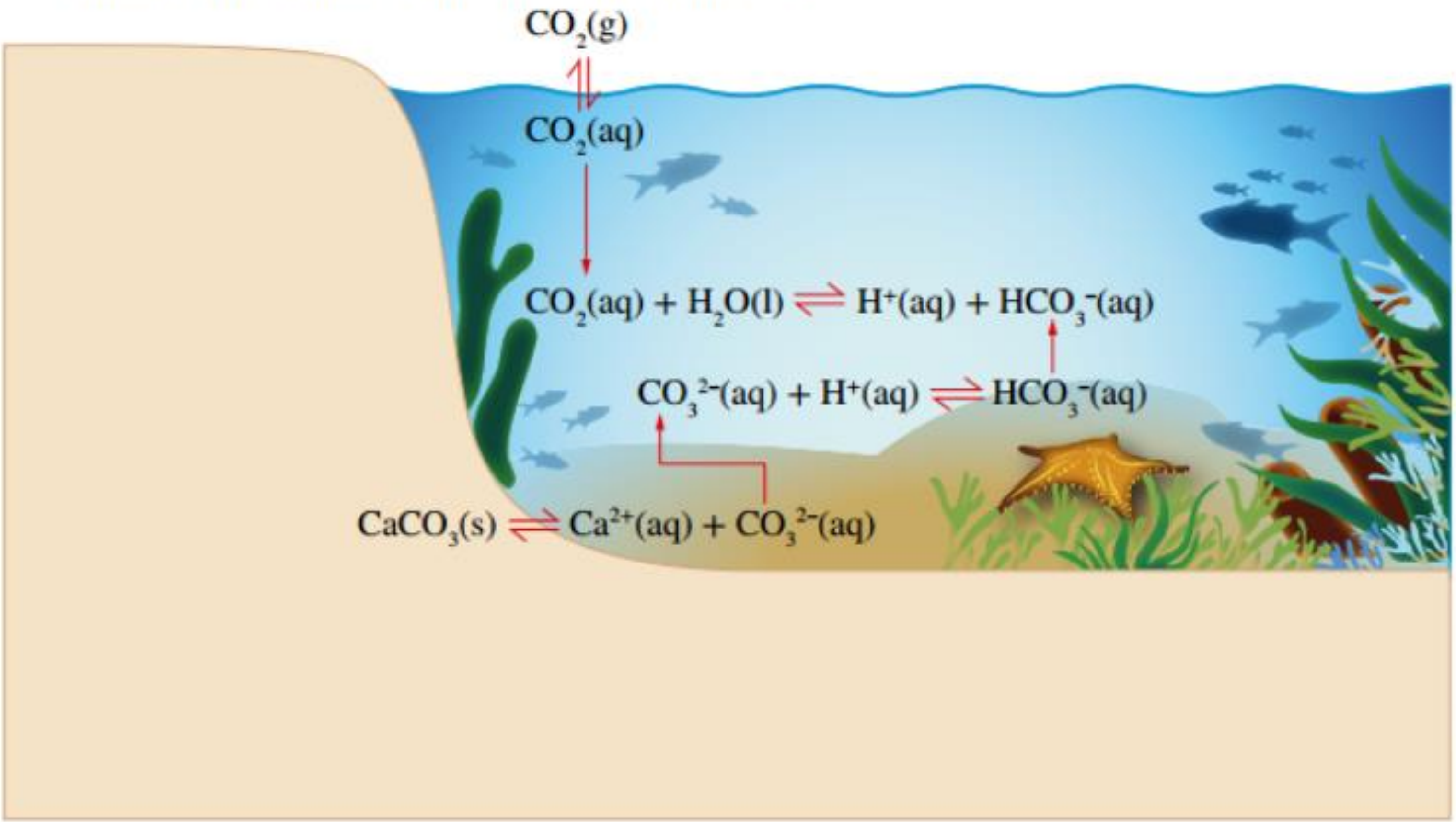
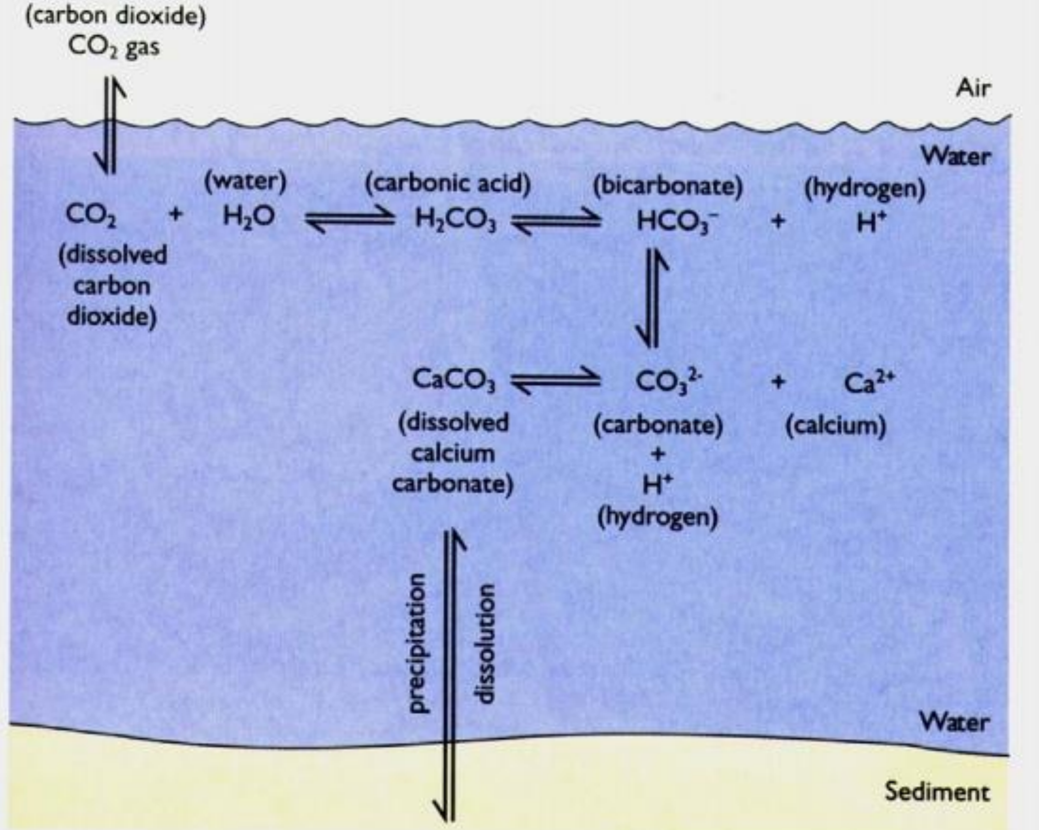


FIGURE 3.2.1 There is an interrelated set of reactions involving carbon in the ocean.



(c) THE CO_2 SYSTEM

Seawater too basic:	$H_2CO_3 \longrightarrow HCO_3^- + H^+$	pH drops
Seawater too acidic:	$HCO_3^- + H^+ \longrightarrow H_2CO_3$	pH rises

(d) CARBONATE BUFFER

The Carbonate Chemistry in Seawater a Buffers System

Effects of Ocean acidification on Sea water

- Increase in H ion concentration
- Decrease in Carbonate ion concentration

$$CO_2\ (gas) + H_2O = H_2CO_3;$$

$$H_2CO_3 = H^+ + HCO_3^-; \quad \text{and}$$

$$HCO_3^- = H^+ + CO_3^{2-}$$