Dissolved Oxygen and Carbon Dioxide

Every atmospheric gas is in equilibrium with that gas dissolved in ocean water. The concentrations of two of these are particularly important. The concentration of oxygen in water is crucial to aquatic animals that depend on dissolved oxygen for respiration. The oceans are a major sink for atmospheric carbon dioxide. However, the oceans are no longer able to absorb the increased concentration of CO_2 in the atmosphere without changes to the acidity levels.

Outline

Henry's Law

When any gas is in contact with water, some gas will dissolve in the water. The amount that dissolves at a particular temperature depends on the pressure, or partial pressure, of the gas. The dissolved gas and the undissolved gas are in equilibrium. For example, let's look at molecular nitrogen in the air. Solvated N_2 is in equilibrium with $N_2(g)$ and water. An equilibrium expression shows this.

$$:N\equiv N:$$

$$N_2(aq) \rightleftharpoons N_2(g) + H_2O(l)$$

$$K_{eq} = \frac{[N_2(g)][H_2O(l)]}{[N_2(aq)]}$$

Because the system is in equilibrium, with rapid forward and reverse reactions, there will be an equilibrium constant that gives us information on the lowest energy state of the system.

The concentration of water is a constant so we can combine it with K_{eq} by dividing both sides of the equation by $[H_2O(l)]$.
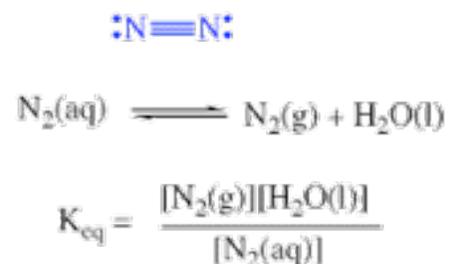
$$\overline{K}_H = \frac{K_{eq}}{[H_2O(l)]} = \frac{P_{N_2}}{[N_2(aq)]}$$

We measure the concentration of a gas-phase molecule by its pressure if it is a pure gas, or by its partial pressure if the gas is part of a gas mixture.

The concentration of any dissolved molecule is given in units of mol/L or molar (M).

Table of Values

Gas	K_H (atm/M)
O_2	769.23
H_2	1282.05
CO_2	29.41
N_2	1639.34

Gas	K_H (atm/M)
He	2702.7
Ne	2222.22
Ar	714.28
CO	1052.63

The data in the table are for the equilibrium between the aqueous gas and the free gas.

$$K_H = P_i/[gas(aq)]$$

To calculate the concentration of the molecule in solution:

$$[gas(aq)] = P_i/K_H$$

Calculations

What is the concentration of N_2 in water under a pure nitrogen atmosphere?

$$K_H = \frac{P_{N_2}}{[N_2(aq)]} \qquad [N_2(aq)] = \frac{P_{N_2}}{K_H} = \frac{1\ atm}{1639.34\ atm/M} = 6.1 \times 10^{-4}\ M$$

What is the concentration of N_2 at the surface of the ocean?

$$P_{N_2} = (0.78)(1.0\ atm)$$

$$[N_2(aq)] = \frac{P_{N_2}}{K_H} = \frac{0.78\ atm}{1639.34\ atm/M} = 4.8 \times 10^{-4}\ M$$

Would the concentration be greater if the total pressure were 5 atm?

$$P_{N_2} = (0.78)(5.0\ atm) = 3.9\ atm$$

$$[N_2(aq)] = \frac{P_{N_2}}{K_H} = \frac{3.9\ atm}{1639.34\ atm/M} = 2.4 \times 10^{-3}\ M$$

Oxygen in Equilibrium

Dissolved Oxygen and Henry's Law

Oxygen dissolved in water can come from the atmosphere or as a byproduct of the photosynthesis of aquatic plants.

For water in equilibrium with the atmosphere, the concentration is governed by Henry's Law, and K_H for O_2 is 769.23. We can calculate the concentration of O_2(aq) to be 0.00027 M.

Water below the air/water interface is not necessarily in equilibrium with the air and can have even less oxygen than this small value. In fact, it is typical for the oxygen concentration in lakes and in the ocean to decrease with depth in the water. Percent saturation is the amount of oxygen in a liter of water relative to the total amount of oxygen that the water can hold at that temperature.

Running water in shallow streams mixes better with air and tends to have a higher oxygen content than still water. There is also a strong temperature dependence on maximum oxygen concentration (see the table below). Atmospheric pressure is lower at higher altitudes so water at higher elevations holds less dissolved oxygen than water at sea level.

The dissolved oxygen levels are higher in the summer and during daylight hours because this is when photosynthetic organisms produce oxygen. Thermal discharges, such as water used to cool machinery in a manufacturing plant or a power plant, raise the temperature of water and lower its oxygen content. Aquatic animals are most vulnerable to lowered dissolved oxygen levels in the early morning on hot summer days when stream flows are low, water temperatures are high, and aquatic plants have not begun producing oxygen.

Temperature (°C)	Dissolved Oxygen (mg/L)	Temperature (°C)	Dissolved Oxygen (mg/L)
0	14.60	23	8.56
1	14.19	24	8.40
2	13.81	25	8.24
3	13.44	26	8.09
4	13.09	27	7.95
5	12.75	28	7.81
6	12.43	29	7.67
7	12.12	30	7.54
8	11.83	31	7.41
9	11.55	32	7.28
10	11.27	33	7.16
11	11.01	34	7.16
12	10.76	35	6.93
13	10.52	36	6.82
14	10.29	37	6.71
15	10.07	38	6.61
16	9.85	39	6.51
17	9.65	40	6.41
18	9.45	41	6.41
19	9.26	42	6.22
20	9.07	43	6.13
21	8.90	44	6.04
22	8.72	45	5.95

Biological Oxygen Demand

This is a measure of the amount of molecular oxygen in milligrams required to convert all the organic molecules contained in 1.0 liter of a water sample to CO_2.

Microorganisms such as bacteria are responsible for decomposing organic waste. When organic matter such as dead plants, leaves, grass clippings, manure, sewage, or even food waste is present in a water supply, the bacteria will begin the process of breaking down this waste. When this happens, much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they need to live. BOD level is a common metric for water pollution.

The BOD level is determined by comparing the dissolved oxygen levels of a water sample before and after 5 days of incubation in the dark. The difference between the two levels represents the amount of oxygen required for the decomposition of any organic material in the sample and is a good approximation of the BOD level.

Unpolluted rivers typically have a BOD below 1 mg/L. Moderately polluted rivers vary between 2 to 8 mg/L. Untreated sewage averages between 200 and 600 mg/L while efficiently treated municipal sewage would be 20 mg/L or less.

Ocean Dead Zones

Nitrogen and phosphorus compounds from agricultural runoff into the oceans causes algae blooms. When the organisms die and decompose, all available dissolved oxygen is used up and the water becomes hypoxic. It can no longer support living things.

Each year, part of the Gulf of Mexico becomes a dead zone that is unable to support fish, shrimp, and other marine life. This is caused by fertilizers that run off fields in the Midwest (Illinois!!), down the Mississippi River to the Gulf.

Carbon Dioxide in Equilibrium

Carbon Dioxide in the Ocean

The levels of carbon dioxide in the atmosphere has been increasing since the beginning of the industrial revolution due to increased combustion of fossil fuels. Much of the carbon dioxide that has been released dissolves in the ocean.

We can use Henry's Law to calculate the concentration of dissolved carbon dioxide in an aqueous solution. The current, average concentration of CO_2 is 387 ppm, that is 387 x 10^{-6} atm.

$$[CO_2] = P/K_H = 3.87 \times 10^{-4} \text{ atm}/29.41 \text{ atm M}^{-1} = 1.32 \times 10^{-5} \text{ M}$$

Dissociation of Carbon Dioxide

Carbon dioxide reacts with water. The carbon atom of CO_2 is electron poor with an oxidation state of IV. The electron rich oxygen of water donates an electron pair to the carbon. After proton transfer from water to an oxygen of the CO_2 unit, carbonic acid is formed.
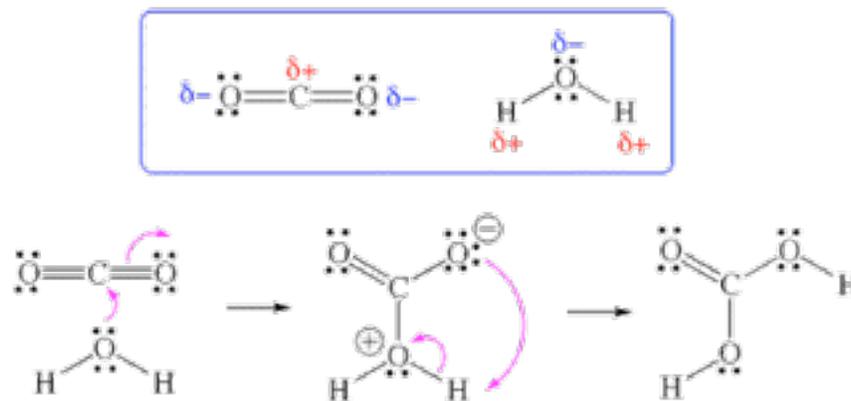
The reaction between water and dissolved carbon dioxide is reversible and rapid.

$$H_2O(l) + CO_2(aq) \rightleftharpoons H_2CO_3(aq)$$

$$K = [H_2O(aq)]K_{eq} = [H_2CO_3(aq)]/[CO_2(aq)]$$

$$K = 1.70 \times 10^{-3}$$

Carbonic acid is in equilibrium with the bicarbonate anion.

$$K_{eq} = \frac{[H^+(aq)][HCO_3^-(aq)]}{[H_2O(l)][H_2CO_3]} \qquad K_a = [H_2O(l)]K_{eq} = \frac{[H^+(aq)][HCO_3^-(aq)]}{[H_2CO_3]} = 2.5 \times 10^{-4}$$

We can combine the two equilibria:

$$CO_2(aq) \rightleftharpoons H_2CO_3(aq) \qquad K_1 = 1.70 \times 10^{-3}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_2 = 2.5 \times 10^{-4}$$

$$CO_2(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{Tot} = K_1 K_2 = 4.25 \times 10^{-7}$$
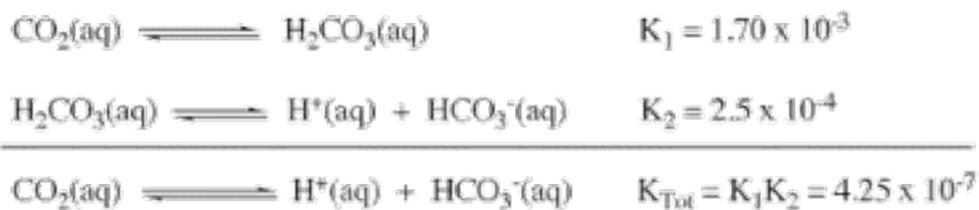
Because the concentration of dissolved carbon dioxide is set by Henry's Law, we can use this to determine the concentration of protons and bicarbonate ion in water.

Temperature Dependence

As with other gases, the solubility of carbon dioxide in water decreases as the temperature increases. You can see this for yourself by observing what happens when you heat a can of soda.

As the temperature of the oceans increases with increasing global temperature (caused by greenhouse gases), carbon dioxide will tend to outgas from the oceans. This will increase the atmospheric concentration of CO_2, causing further increases in temperature of the atmosphere, etc.