Carbon Dioxide and Carbonic Acid

Sometimes lost in the climate arguments is the fact that atmospheric CO_2 is crucial to life on Earth. Without it, global average temperature would be about -18°C, well below freezing. Instead, global average temperature is closer to +15°C- quite comfortable for life. Also, obviously, plants need CO_2 in the atmosphere to live. They use it, water, and sunlight for photosynthesis to produce organic matter (food) that supports the rest of us.

There are effects of atmospheric CO_2 that are not climate related, but which may play a role in feedback systems. These effects include the chemical weathering of rocks and minerals. Here, we point out the effects of dissolution of gas-phase (vapor) CO_2 in water. This is one of the first things that any geochemistry student has to learn!

CO_2 dissolves in water to form a weak acid (carbonic acid) according to:

$$CO_{2\,(gas)} + H_2O_{(liquid)} \rightarrow H_2CO_{3\,(dissolved)} \qquad (1)$$

In chemistry, there is a law called the law of mass action. Imagine that we have a little chamber filled with CO_2 gas, into which we put a beaker of water. The CO_2 gas will dissolve in the water until "equilibrium" is reached. At "equilibrium", no more net reaction takes place. The water has absorbed all of the CO_2 that it can absorb, and is now "saturated" and won't hold any more in the dissolved form. At equilibrium, the rate of CO_2 dissolution in water is exactly equal to the rate of CO_2 exsolution back into the gaseous state. For such chemical reactions, chemists have found that equations of the following type describe the situation at chemical equilibrium:

$$K_H = \frac{\left[H_2CO_3\right]}{P_{CO_2}\left[H_2O\right]} \qquad (2)$$

In equation 2, $\left[H_2CO_3\right]$ is the "active concentration" of carbonic acid in the water, P_{CO_2} is the partial pressure of CO_2 gas, K_H is a constant called the "Henry's Law constant for CO_2 dissolving in water" (i.e., it's just a number that describes the particular properties of CO_2 dissolving in water- the number would be different for CO_2 dissolving in, say, alcohol!), and $\left[H_2O\right]$ is the concentration of water in water (because the concentration of water in water is always the same, chemists set things up so that the equation works if $\left[H_2O\right] = 1$).

Equation 2 can be algebraically rearranged to:

$$\left[H_2CO_3\right] = K_H P_{CO_2} \qquad (3)$$

This assumes that $\left[H_2O\right] = 1$, as we said above, and shows that for a given partial pressure of CO_2, there is a definite concentration of H_2CO_3 in water that is in equilibrium with the air. Carbonic acid, being an acid, undergoes what is called dissociation:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (4)$$

The equilibrium constant for reaction 4, called K_1 (for "first dissociation constant"), is simply:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

That is, H_2CO_3 dissociates into an H^+ cation and a bicarbonate (HCO_3^-) anion (remember, these are ions dissolved in water). This reaction causes H^+ to be released, which makes the water slightly acidic. We measure acidity using the "pH" scale. You may have heard of the 1-to-14 pH scale in which neutral is 7, acid conditions correspond to pH values of less than 7, and basic or caustic conditions correspond to pH values greater than 7. In fact, pH means "the negative of the logarithm of the active concentration of H^+ in the water", or put mathematically,

$$pH = -\log[H^+] \qquad (5)$$

By this definition, a pH of 2 means that there is a concentration of H^+ in the water of 10^{-2} moles of H^+ per liter of water. Why is neutral at a pH of 7? Think of "pure" water; it turns out that there is no such thing! Water itself dissociates (remember equation 4) to:

$$H_2O \rightarrow H^+ + OH^- \qquad (6)$$

So that there is always some H^+ and OH^- (hydroxyl) in "pure" water. There is also an equilibrium constant that characterizes reaction 6:

$$K_w = [H^+][OH^-] = 10^{-14}$$

Put another way, "pure" water with no added acid or base will have a pH of 7 (which means that $[H^+] = 10^{-7}$ moles per liter (M) and $[OH^-] = 10^{-7}$ M).

In the above equations,

$K_w = 10^{-14}$

$K_H = 10^{-1.5}$

$P_{CO2(atm)} = 10^{-3.5}$ atm

$K_1 = [H^+][HCO_3^-]/[H_2CO_3] = 10^{-6.4}$

Given all this information, calculate what the pH of pure water in equilibrium with atmospheric CO_2. Follow along on the board, making notes below, as I give pointers on the board.