Buffers Workshop Bonus: Background

When you exhale, you emit a significant amount of carbon dioxide in the gas phase, $CO_2(g)$. Consider blowing through a straw into water. You are mixing carbon dioxide with water. The $CO_2(g)$ solvolyzes in water to form $CO_2(aq)$, which is shown in Step 1) below. The hydrated form, $CO_2(aq)$, is in equilibrium with carbonic acid, which is shown in Step 2). Carbonic acid dissociates to bicarbonate ion, Step 3), and bicarbonate ion dissociates to carbonate ion, Step 4). All four of these steps are part of the overall system at equilibrium. In blood and seawater, Step 3) is the critical equilibrium reaction. However, in complex systems such as human blood and the oceans, other external factors play important roles and may affect one or more of the other steps, the overall equilibrium, and have a very profound effect on the pH of the buffered system. In these cases, the dynamics of the system and all four steps must be considered applying Le Chatelier's principles in order to explain the observed pH.

1) $H_2O(l) + CO_2(g) \rightleftharpoons CO_2(aq)$ K_1
2) $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ K_2
3) $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K_3 = 4.2 \times 10^{-7} = K_{a_1}$
4) $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $K_4 = 4.8 \times 10^{-11} = K_{a_2}$

$K_1 \times K_2 = 1.3 \times 10^{-3}$

Blood

The pH of human blood has a "normal range" of 7.35-7.45. Blood buffers must effectively function between a pH range of 7.2 to 7.4. If the pH of blood drops below 6.8 or rises above 7.8, death may occur.

The blood's carbonic acid / bicarbonate buffer system is dynamic and not reliant solely on the acid-base properties of the bicarbonate and carbonic acid equilibrium alone, Step 3), but also catalysis, the relative rates of reaction, and hydrogen ion concentration changes affected by other ions, molecules, and physical/chemical processes.

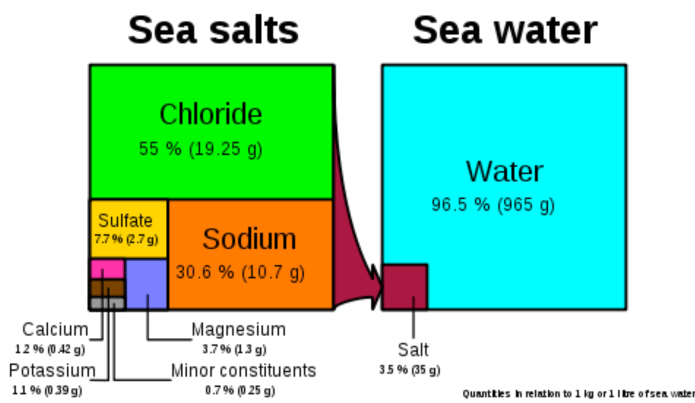
The buffering power of the bicarbonate system in blood involves several organs and physiological processes. The principal two are the kidneys and renal system, which remove $H^+ + HCO_3^-$ through urine, and the lungs and respiratory system through breathing, complemented by the catalytic effects of an enzyme, carbonic anhydrase, on Step 2) and Step 3) which affects $[CO_2(aq)]$. Although carbonate ion is involved in bone formation and is removed from the system, it occurs on a very slow time scale and Step 4) does not appreciably impact the dynamics of the system. Therefore, the pH of the blood buffer system is determined principally by K_1, K_2, and K_3:

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O \rightleftharpoons CO_2(g)$$

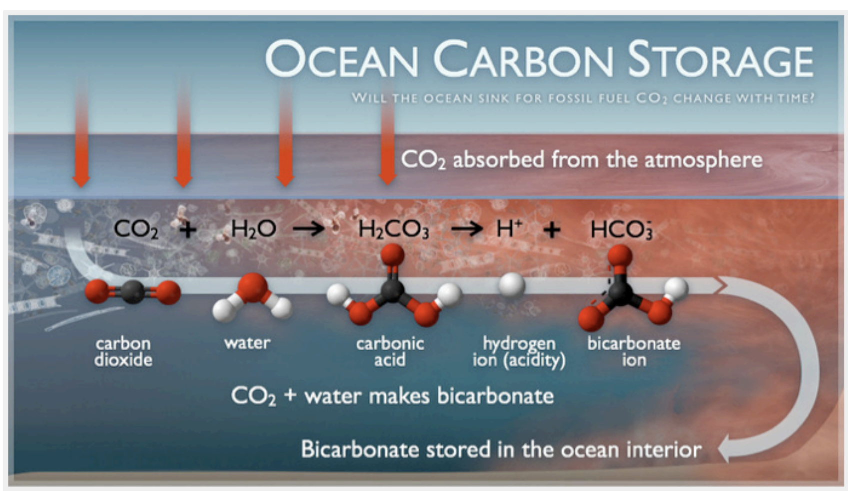
$K_1 = [CO_2(aq)] / [CO_2(g)]$
$K_2 = [H_2CO_3(aq)] / [CO_2(aq)]$
$K_3 = [H^+(aq)]\ [HCO_3^-(aq)] / [H_2CO_3(aq)]$
where $CO_2(aq)$=dissolved CO_2 and $CO_2(g)$ = gaseous CO_2

Oceans

Just as blowing through a straw introduces carbon dioxide into water, the turbulence at the oceans' surface helps solvate (dissolve) atmospheric CO_2, Step 1). In considering the bicarbonate buffer and pH of blood, it was possible to neglect other materials dissolved in blood to develop a reasonable explanation, however the oceans' pH is an even more complicated system since there are other ions, which affect pH, plus temperature and pressure dependent variables that also must be considered.



Although the physical/chemical properties are complicated, the system and its dynamics had been in relative stasis (@ equilibrium) since ancient times, and the ocean's pH in its upper reaches a relatively constant (~8.1 to 8.2). However, the system's carbon balance is being perturbed and the dynamics of the system and all of the Steps 1) to 4) must be considered applying Le Chatelier's principles in order to explain the observed changes in pH.



http://i2i.stanford.edu/AcidOcean/AcidOcean.htm