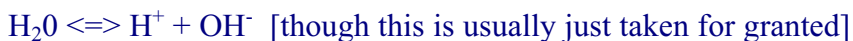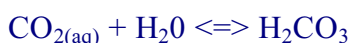# Carbonate buffers

Theory

A classic buffer is a combination of a weak acid and its conjugate salt; for instance, carbonic acid (H_2CO_3) and sodium bicarbonate ($NaHCO_3$), or even sodium bicarbonate and calcium carbonate. What happens when you titrate this combination with the (strong) acid of your choice? Well, in any buffer system, the boost in [H^+] increases the reaction rate H^+ + salt => weak acid and takes some H^+ out of circulation.

Of course, as it does so, it increases weak acid concentration, so the reverse reaction rate starts to increase until you get a new equilibrium. Similarly, titration with a strong base decreases the H^+ + salt => weak acid rate, and so (since the weak acid dissociation is still happening), the weak acid => H^+ + salt adds some H^+ to the solution. Thus the pH changes less than it would if you titrated pure water - it's buffered.

The major reactions involved in the carbonate system are:

$CO_{2(aq)}$ <=> CO_2 (gas) [i.e., little fizzy bubbles and the atmosphere]

$CO_{2(aq)}$ + H_2O <=> H_2CO_3

H_2CO_3 <=> H^+ + HCO_3^- [or you can pretend the H^+ turns into H_3O^+ if you like]

HCO_3^- <=> H^+ + CO_3^{2-}

XCO_3 <=> X^{2+} + CO_3^{2-} [e.g., $CaCO_3$; this is why limestone affects pH]

$XHCO_3$ <=> X^+ + HCO_3^- [e.g., $NaHCO_3$]

H_2O <=> H^+ + OH^- [though this is usually just taken for granted]

The major thing to keep in mind is that all of these reactions run constantly in both directions. All other things being constant, (a big "if", but there you are), the reaction rates are proportional to the product(s) of the concentrations of reactants. (You'll note that this may be constant in the case of things like $CaCO_3$ sitting in a lump on the bottom of the flask, or CO_2 floating around at constant pressure in the atmosphere above the flask.)

If the weak acid and conjugate salt are the only things in solution, the pH is determined by the ratio of acid to salt (this is the source of tables relating pK, [CO_2] and pH). You can get significant buffering out to about a 100:1 ratio, so most buffer systems will work over a total range of about 4 pH units; they work best, of course, near the middle of their range. Thus, for the carbonate system we're worried about here, if you want to keep the same pH, but halve or double the KH, you would expect to halve or double [CO_2] to keep the same ratio and the same equilibrium pH.

The easiest way to calculate the pH, based on selected ion concentrations is the Henderson-Hasselbalch equation. It is based on the constant equilibrium.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad (1)$$
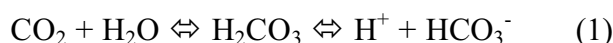
$$K = \frac{[H^+][HCO_3^+]}{[CO_2][H_2O]} \qquad (2)$$

Because water is in excess, its concentration can be set as 1. This results in the following equation:

$$[H^+] = K \cdot \frac{[CO_2]}{[HCO_3^+]} \qquad (3)$$

The logarithmic form of the mathematical term (3) is the Henderson-Hasselbalch equation:

$$pH = pK + \log \frac{[CO_2]}{[HCO_3^+]} \qquad (4)$$

A useful tool to predict the resulting pH, which depends on carbon dioxide and/or hydrogen carbonate concentrations, can be found at http://www.tmc.tulane.edu/departments/anesthesiology/acid/henderson.html.

Experimental

Dissolve the amount of sodium hydrogen carbonate needed (or calculated by you) in demineralized water and purge a mixture of CO_2/N_2 in the desired proportions through it.
Example: If you dissolve 10 mM/l $NaHCO_3$ and purge a mixture CO_2/N_2 10%/90% through it, you will get a pH of 6.9.

Another possibility: Dissolve sodium carbonate and sodium hydrogen carbonate in certain proportions in demineralized water.

Literature

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- Stumm, W. and J.J. Morgan 1981. Aquatic Chemistry, Wiley Interscience, 2nd edition, 171-229