How to calculate pH in a solution made by dissolving $NaHCO_3$

A buffer is a solution that has the ability to keep pH within a certain and narrow range even when hydrogen ions (H^+) or hydroxide ions (OH^-) are added to the solution. In other words: buffers resist changes in pH when either H^+ or OH^- is added to the buffer solution. If much H^+ or OH^- is added to the solution the buffer may not be able a significant change in pH.

There are many examples of buffers:

Blood in humans is a well buffered system buffered by several buffers such as $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} and bicarbonate H_2CO_3/CO_2, HCO_3^- and CO_3^{2-}.

Seawater is a buffer and is buffered around pH=8.4, mainly because of sodium bicarbonate.

Example:

Consider a solution made of 0.1 M $NaHCO_3$. The sodium bicarbonate will dissolve into Na^+ and HCO_3^-. Furthermore, the HCO_3^- will partly split into fractions of CO_2 and CO_3^{2-}, respectively depending on pH. First of all we should start by finding out what will happen to $NaHCO_3$ when it dissolves in water.

This is easier that it might seem. We simply use the fact that the charge balance is always zero in an aqueous solution.

From the pdf document about equilibrium we know how to calculate the $[CO_2]$, $[HCO_3^-]$ and $[CO_3^{2-}]$. In fact it is not necessary to calculate the $[CO_2]$ but to help understand what is going on, it's included in the following calculations that can also be seen in an excel spreadsheet (can be downloaded from the webpage)

From the pdf document about equilibriums we have that:

Compound or ion	Calculation
$[CO_2]^*$	$\dfrac{[TIC]}{1+\dfrac{K_a^{CO_2^*}}{[H^+]}+\dfrac{K_a^{CO_2^*}\cdot K_a^{HCO_3^-}}{[H^+]^2}}$
$[HCO_3^-]$	$\dfrac{[TIC]}{1+\dfrac{[H^+]}{K_a^{CO_2^*}}+\dfrac{K_a^{HCO_3^-}}{[H^+]}}$
$[CO_3^{2-}]$	$\dfrac{[TIC]}{1+\dfrac{[H^+]^2}{K_a^{CO_2^*}\cdot K_a^{HCO_3^-}}+\dfrac{[H^+]}{K_a^{HCO_3^-}}}$

In the case we are adding 0.1 M $NaHCO_3$ we are adding 0.1 M Na^+ and 0.1 M HCO_3 that is distributed among CO_2^*, HCO_3^- and CO_3^{2-} depending on pH. This pH or $[H^+]$ is easily calculated (not considering ionic strength).

Step 1: A charge balance is established

It must be that $[Na^+] - [HCO_3^-] - 2\cdot[CO_3^{2-}] = 0$ in the sodium bicarbonate solution.

If not, the charge balance is not zero and something is wrong. This equation can be fine-tuned to include $[H^+]$ and $[OH^-]$ so that the equations is:

$[Na^+] - [HCO_3^-] - 2\cdot[CO_3^{2-}] + [H^+] - [OH^-] = 0$

In the excel spreadsheet this latter equation is used.

We do not know either the $[HCO_3^-]$ or the $[CO_3^{2-}]$ as the $[H^+]$ is unknown.

However, by trying out with the different $[H^+]$'s in the equation:

$$[Na^+] + [H^+] - [OH^-] - \frac{[TIC]}{1+\dfrac{[H^+]}{K_a^{CO_2^*}}+\dfrac{K_a^{HCO_3^-}}{[H^+]}} - 2\cdot\frac{[TIC]}{1+\dfrac{[H^+]^2}{K_a^{CO_2^*}\cdot K_a^{HCO_3^-}}+\dfrac{[H^+]}{K_a^{HCO_3^-}}} = 0.$$

From the excel spreadsheet it can be seen that when $[H^+]$ is $10^{-8.31}$ the equation is fulfilled.

The conclusion is that a 0.1 M $NaHCO_3$ has a pH of 8.31.

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