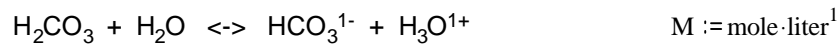


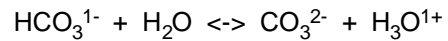
# Introduction to Polyprotic Acids

For this example we will study the equilibrium of carbonic acid ( $\text{H}_2\text{CO}_3$ ) in water. This is a very important equilibrium in natural systems because the carbonate buffer is important for living organisms and this equilibrium controls the uptake of  $\text{CO}_2$  by the ocean. This is a major global sink for  $\text{CO}_2$  that helps to keep the greenhouse effect in balance.

First the equilibrium involved:

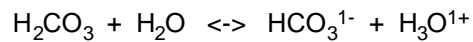


$$K_{a1} = \frac{(C_{\text{HCO}_3}) \cdot (C_{\text{H}_3\text{O}})}{(C_{\text{H}_2\text{CO}_3})} \quad K_{a1} := 4.3 \cdot 10^{-7} \cdot \text{M}$$



$$K_{a2} = \frac{(C_{\text{CO}_3}) \cdot (C_{\text{H}_3\text{O}})}{(C_{\text{HCO}_3})} \quad K_{a2} := 5.61 \cdot 10^{-11} \cdot \text{M}$$

For a solution that is 0.1 M in  $\text{H}_2\text{CO}_3$ . Start with the first equilibrium:



Initial	0.1 · M	0 · M	0 · M
Change	- X	X	X
Final	0.1 - X	X	X

So that at equilibrium:

$$K_{a1} = \frac{(X) \cdot (X)}{0.1 - X}$$

Assume that  $\text{H}_2\text{CO}_3$  is unchanged so that

$$K_{a1} = \frac{X^2}{0.1}$$

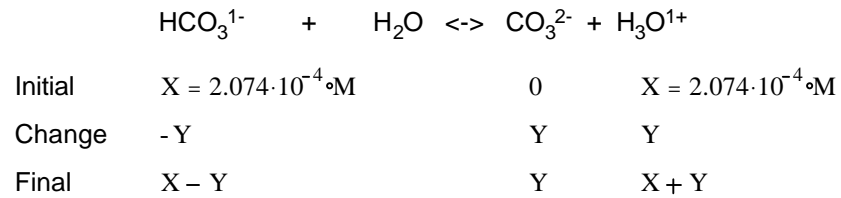
$$X := \sqrt{K_{a1} \cdot 0.1 \cdot \text{M}}$$

$$X = 2.074 \cdot 10^{-4} \cdot \text{M}$$

This gives the following concentrations from the first equilibrium

$$\begin{array}{ll}
 C_{\text{H}_2\text{CO}_3} := 0.1 \cdot \text{M} - X & C_{\text{H}_2\text{CO}_3} = 0.1 \cdot \text{M} \\
 C_{\text{HCO}_3} := X & C_{\text{HCO}_3} = 2.074 \cdot 10^{-4} \cdot \text{M} \\
 C_{\text{H}_3\text{O}} := X & C_{\text{H}_3\text{O}} = 2.074 \cdot 10^{-4} \cdot \text{M}
 \end{array}$$

Now for the second equilibrium



So that at equilibrium:

$$K_{a2} = \frac{(Y) \cdot (2.07 \cdot 10^{-4} + Y)}{2.07 \cdot 10^{-4} - Y}$$

Assume that HCO3 and H3O is unchanged so that

$$K_{a2} = \frac{(Y) \cdot (2.07 \cdot 10^{-4})}{2.07 \cdot 10^{-4}}$$

$$Y := K_{a2}$$

$$Y = 5.61 \cdot 10^{-11} \cdot \text{M}$$

This gives final concentrations for each species as:

$$\begin{array}{ll}
 C_{\text{H}_2\text{CO}_3} := 0.1 \cdot \text{M} - X - Y & C_{\text{H}_2\text{CO}_3} = 0.1 \cdot \text{M} \\
 C_{\text{HCO}_3} := X - Y & C_{\text{HCO}_3} = 2.074 \cdot 10^{-4} \cdot \text{M} \\
 C_{\text{CO}_3} := Y & C_{\text{CO}_3} = 5.61 \cdot 10^{-11} \cdot \text{M} \\
 C_{\text{H}_3\text{O}} := X + Y & C_{\text{H}_3\text{O}} = 2.074 \cdot 10^{-4} \cdot \text{M} \\
 \text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1}) & \text{pH} = 3.683
 \end{array}$$

Practice Problem. 10.0 mL of 5 M acetic acid is diluted to 500.0 mL with deionized water. What is the concentration of each species in the final solution?

The acid dissociation constant for acetic acid:

$$K_a := 1.8 \cdot 10^{-5} \cdot M$$

The initial concentration of the solution

$$C_{\text{stock}} := 5 \cdot M$$

$$V_{\text{stock}} := 10.0 \cdot \text{mL}$$

$$V_{\text{total}} := 500.0 \cdot \text{mL}$$

$$C_{\text{acid}} := \frac{C_{\text{stock}} \cdot V_{\text{stock}}}{V_{\text{total}}}$$

$$C_{\text{acid}} = 0.1 \cdot M$$

The equilibrium solution for	HA	+	H <sub>2</sub> O	$\leftrightarrow$	H <sub>3</sub> O <sup>+</sup>	+	A <sup>-</sup>
Initial Concentration	$C_{\text{acid}}$						
Equilibrium Concentration	$C_{\text{acid}} - X$				X		X

Equilibrium expression:

$$K_a = \frac{X^2}{C_{\text{acid}} - X}$$

Assuming X is smaller than [acid], this reduces to:

$$K_a = \frac{X^2}{C_{\text{acid}}}$$

Solving for X:

$$X := \sqrt{K_a \cdot C_{\text{acid}}}$$

$$X = 1.3416 \cdot 10^{-3} \cdot M$$

Equilibrium Concentrations:

$$C_{\text{HA}} := C_{\text{acid}} - X$$

$$C_{\text{HA}} = 0.099 \cdot \text{M}$$

$$C_{\text{H3O}} := X$$

$$C_{\text{H3O}} = 1.342 \cdot 10^{-3} \cdot \text{M}$$

$$C_{\text{A}} := X$$

$$C_{\text{A}} = 1.342 \cdot 10^{-3} \cdot \text{M}$$

$$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$$

$$\text{pH} = 2.872$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = 11.128$$

Solving for X without assumptions:

$$K_a = \frac{X^2}{C_{\text{acid}} - X}$$

$$X := \left[ \begin{array}{l} \frac{-1}{2} \cdot K_a + \frac{1}{2} \cdot \sqrt{K_a^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \\ \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot \sqrt{K_a^2 + 4 \cdot K_a \cdot C_{\text{acid}}} \end{array} \right]$$

$$X = \left[ \begin{array}{l} 1.3327 \cdot 10^{-3} \\ -1.3507 \cdot 10^{-3} \end{array} \right] \cdot \text{M}$$

Equilibrium Concentrations (Calculated for both roots, select the reasonable answer [top or bottom in ()]):

$$C_{\text{HA}} := C_{\text{acid}} - X$$

$$C_{\text{HA}} = \left[ \begin{array}{l} 0.099 \\ 0.101 \end{array} \right] \cdot \text{M}$$

$$C_{\text{H3O}} := X$$

$$C_{\text{H3O}} = \left[ \begin{array}{l} 1.333 \cdot 10^{-3} \\ -1.351 \cdot 10^{-3} \end{array} \right] \cdot \text{M}$$

$$C_{\text{A}} := X$$

$$C_{\text{A}} = \left[ \begin{array}{l} 1.333 \cdot 10^{-3} \\ -1.351 \cdot 10^{-3} \end{array} \right] \cdot \text{M}$$

$$i := 0, 1..1$$

$$\text{pH}_i := -\log(C_{\text{H3O}_i} \cdot \text{M}^{-1})$$

$$\text{pH} = \left[ \begin{array}{l} 2.875 \\ 2.869 - 1.364i \end{array} \right]$$

$$\text{pOH} := 14 - \text{pH}$$

$$\text{pOH} = \left[ \begin{array}{l} 11.125 \\ 11.131 + 1.364i \end{array} \right]$$