Polyprotic Acids

By now we should be pretty comfortable dealing with monoprotic acids like:

HCl HNO_3

$HClO_4$ CH_3COOH

$^{+}HNH_3$

Each of these acids has a single proton to offer to the system. Consequently there is a nice one-to-one stoichiometry to deal with (one mole of acid yields one mole of protons). The chemical equilibria are also pretty easy.

You either have the strong acid case in which we assume everything goes to completion and what we start with is what we end with:

	HCl	$\rightarrow$	H^+	+	Cl^-
start	100%		0		0
equil.	0		100%	100%	

or we have the the weak acid case where very little dissociation occurs, the equilibrium constant, Ka, is very small, and basically, nothing happens (though that doesn't stop us from calculating the pH of the weak acid):

	HA	$\Leftrightarrow$	H^+	+	A^-
initial	C_{HA}		0		0
change	-x		+x		+x
equil.	C_{HA}-x		x		x

And from the RICE expression we can easily derive the simplified equations for acids (and their base complements) that pretty much estimate the pH of any monoprotic acid or basic solution:

$[H^+] = Ca$ for strong acids $[H^+] = (K_aC_a)^{0.5}$ for weak acids $[H+] = K_aC_a/C_b$ for buffers

If only that was all there was to it.

To complicate matters, some acids and bases are more fortunate than others in that they are given multiple reactive sites at birth. These molecules are known as polyprotic acids and bases and include:

diprotic acids and bases $Ba(OH)_2$ H_2SO_4

$^+H_3NCHCO_2H$ H_2CO_3 $HOOCCH_2COOH$

triprotic acids H_3PO_4

tetraprotic acids $(HOOCCH_2)_2\text{-}NCH_2CH_2N\text{-}(HOOCCH_2)_2$

Obviously polyprotic systems are more problems to deal with. First the stoichiometry is not a simple one-to-one correspondence and we have to start being careful to account for multiple protons or hydroxides when they are thrown in solution (for example, the two hydroxides on $Ba(OH)_2$.

Also, from an equilibrium stand point, we have to recognize that each proton or hydroxide in the molecule had its own acid/base strength which can be defined in terms of its equilibrium constant. Thus if we have a molecule with three protons, there will be three acid base equilibria with their own equilibrium constants, K_{a1}, K_{a2}, K_{a3}.

Understand that because each of these protons has its own affinity for a base, we do not consider the loss of protons to occur indiscriminately or all at once over the molecule. Instead, there is a nice systematic series of reactions with the first reaction involving the most acidic proton, the resulting conjugate base reacting to yield the next most acidic proton, and so on.

This is actually good news because it means we can talk about the equilibria separately.

So let's write the equilibria down in sequence for the general case of a triprotic acid, H_3A, including equilibrium equations:

1) $H_3A \Leftrightarrow H^+ + H_2A^-$ $\qquad Ka_1 = \dfrac{[H^+][H_2A^-]}{[H_3A]}$

(most acidic acid)

2) $H_2A^- \Leftrightarrow H^+ + HA^{2-}$ $\qquad Ka_2 = \dfrac{[\quad H^+][HA^{-2}]}{[H_2A^-]}$

3) $HA^{-2} \Leftrightarrow H^+ + A^{3-}$ $\qquad Ka_3 = \dfrac{[H^+][A^{-3}]}{[HA^{-2}]}$

(least acidic acid)

Now you might ask which acid is strongest: H_3A or H_2A^- or HA^{-2}

And the answer is : H_3A.

Which means that if I tell you that the K_a values are 10^{-3}, 10^{-7} and 10^{-11} for a triprotic acid, you know that:

- the K_{a1} for H_3A is 10^{-3}
- the K_{a2} for H_2A^- is 10^{-7}
- the K_{a3} for $HA^{=}$ is 10^{-11}

and if you are looking for a reason why chemically, here are a couple:

1. the most acidic species will be the one with the most protons and the least acidic species will be the one with the fewest protons
2. in ranking Ka values, it makes sense that the largest value numerically will correspond to the acid most wanting to get rid of protons (the one with the most positive charge in the form of protons) and the smallest value numerically will be the acid that has the most negative charge and therefore most wants to hold on to a proton.

But you needn't think about it too hard—very simply, the species with the most protons has the largest Ka value.

Polyprotic acid calculations:

From a perspective in which we would want to work acid/base problems, the important thing to look for in polyprotic acids is whether the K_a values are really far apart in size. This is of interest to you because:

> **When K values in a polyprotic system are 3 or more orders of magnitude apart, we can treat the chemical problem as involving cases of single equilibria.**

In other words, we can treat most diprotic and triprotic acid systems as just a collection of monoprotic acids to which we can apply all the stuff we've learned the last couple of lectures.

$[H^+] = Ca$ for strong acids $\quad$ $[H^+] = (K_aC_a)^{0.5}$ for weak acids $\quad$ $[H+] = K_aC_a/C_b$ for buffers

There is one exception among the calculations and that is for what we call the amphiprotic acid case, and we will see that in a moment. But first, let's consider the simpler calculations for polyprotic acids by specifically looking at the diprotic acid, carbonic acid: H_2CO_3

Here are the two equilibria

1) $H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$ $\qquad$ $Ka_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} = 1 \times 10^{-5}$

2) $HCO_3^- \Leftrightarrow H^+ + CO_3^{-2}$ $\qquad$ $Ka_2 = \dfrac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = 1 \times 10^{-11}$

(By the way carbonic acid equilibria are famous because they explain everything from why Diet Coke is acidic to why Tums are good for an upset stomach to why Round Rock water spots your dishes and your car to why I can write on the board with chalk.)

All that is left to do then, is make sure we choose the right equilibrium to solve a problem.

As we look at the word problems, let’s make things easier for ourselves by visualizing all the possible beakers containing forms of a diprotic acid and think about where we are on a titration curve if we were titrating a weak diprotic acid with a strong base.:

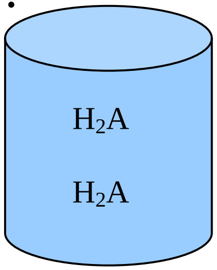
Case 1. What is the pH of a 0.1 M H_2CO_3 solution with $K_{a1} = 10^{-5}$?

Where are you on a titration curve? Beginning of weak acid titration

Equation used to determine the pH. $H^+ = (K_{a1}C_a)^{0.5}$

Approximate pH. 3

Which is what you would expect for a weak acid.



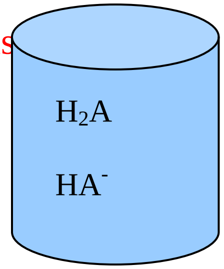
Case 2. What is the pH of a 0.1 M H_2CO_3 solution mixed with 0.1 M $NaHCO_3$ with $K_{a1} = 10^{-5}$?

Where are you on a titration curve? In the buffer region for the first dis

Equation used to determine the pH. $H^+ = K_{a1}C_a/C_b$

Approximate pH. 5

Which is what you would expect for a weak acid buffer.

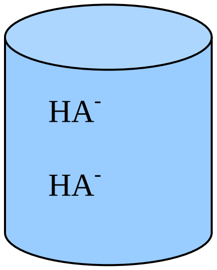


Case 3. What is the pH of a 0.1 M $NaHCO_3$ (the most famous antacid)with $K_{a1} = 10^{-5}$ and $K_{a2} = 10^{-11}$

Where are you on a titration curve? At the first equivalence point.

Equation used to determine the pH. $H^+ = (K_{a1}\ K_{a2})^{0.5}$

Approximate pH. 8



Which is what you would expect as we have formed a base and the pH jumps considerably.

Note!!!! HA^- is a special compound because it can behave both as an acid and as a base. As an acid, it donates a proton according to K_{a2} . But it is also a base because it is the conjugate base formed when deprotonation occurs for $K_{a1.}$ If you want proof that it is a switch hitter, look in the two equations for carbonic acid. It is in both chemical equilibria. It is not surprising then that:

- that we refer to this kind of compound as amphiprotic (or a switch hitter in some circles)
- that we would need both K values in the equation used to calculate its pH (the amphiprotic acid equation)
- when you tell your grandmother that Rolaids is a switchhitter that she will wonder what they are teaching in college these days

$$H^+ = (K_{a1}\ K_{a2})^{0.5}$$

I could easily derive the amphiprotic equation by combining the two equilibria and making some approximations, but I prefer that you just trust me on this, and we can move on.

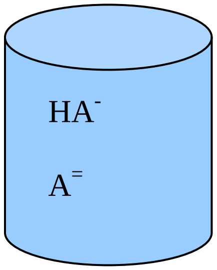
Back to normal stuff:

Case 4. What is the pH of a 0.1 M $NaHCO_3$ mixed with 0.1 M Na_2CO_3 with $K_{a2} = 10^{-11}$

Where are you on a titration curve? In the second buffer region.

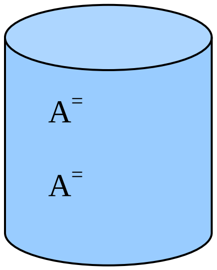
Equation used to determine the pH. $H^+ = K_{a2}C_a/C_b$

Approximate pH. 11



Which makes sense since our K_a value is pretty high

Case 5. What is the pH of a 0.1 M 0.1 M Na_2CO_3 with $K_{a2} = 10^{-11}$



Where are you on a titration curve? At the second end point.

Equation used to determine the pH. This is a weak base
So we use the weak base equation: $OH^- = (K_bC_b)^{0.5}$

Approximate pOH 2 and pH 12

Which makes sense since our K_b value is pretty large.

Generalizing our calculation for a polyprotic acid: there are three different kinds of calculations you perform

- Weak acid and weak base approximations at the beginning and the end of the titration when you are either fully protonated or deprotonated.
- Buffers calculations when you have both an acid and its conjugate base in solution—note that diprotic acids have two buffers, triprotic acids have three buffer regions, etc.
- Amphiprotic calculations happen when you have a species capable of both adding and losing a proton. These compounds need two equilibrium expressions to explain them which is why they are the only equations so far in our work to require two equilibrium constants.

Now go work the triprotic example in worksheet 7. It is just like this but far more painful and it needs to get done if you are going to do these problems on an exam.