Lecture 10: Water Equilibria Part III--Solving the weak acid and weak base cases.

This is our third lecture on acid base water chemistry. In the first one we learned about the temperature dependent calculation of pH from Kw for pure water. In the second lecture we learned that strong electrolytes dissociate completely in water and if those strong electrolytes include strong acids or strong bases, it is easy to estimate a pH since the amount of proton or hydroxide in solution is simply the amount of strong acid or strong base that you added to solution initially.

Today's lecture looks at a third case in which you throw a weak acid or base into solution and predict the pH. Once again we will be using the RICE expression and will now derive the weak acid or weak base equations from it. Things will be a little more complicated and will require that we make a few assumptions in order to yield a really simple equation to find the pH of the solution. But in the end, we use the same theoretical foundation involving chemical equilibria from Chapter 9.

Time out for nomenclature of weak acids and bases.

There are an infinite number of weak acid or weak base compounds that we can draw, and it doesn't take long before some of them look so complicated that we think we can't even begin to solve the calculation. But what is most important to note is that weak acids and weak bases are based on the combination of two simple parts

a conjugate base that is either charged or uncharged (A^- or B) and is in all weak bases and acids
a proton (H^+) that is attached to the weak base to form a weak acid.

So no matter how complicated the structure, we will see that we can always write simple equilbria expressions that involve

B	A^-	BH^+	HA
a neutral weak base	a charged weak base	a charged weak acid	a neutral weak acid

For this lecture we will work with the form with which you are most familiar:

$HA \rightleftharpoons H^+ + A^-$ that has $K_a = [H^+][A^-]/[HA]$

We will see shortly that the RICE expression solution for this weak acid equilibria is simply

So from now on, when you see a nasty looking chemical compound that is a weak acid, some odd sounding name like hydrocyanic acid or some odd looking structure like $(CH_3)_3CH_2CH_2CH_2CH_2CH_2COOH$, if you know it is a weak acid, then simply assign the HA notation to it and use

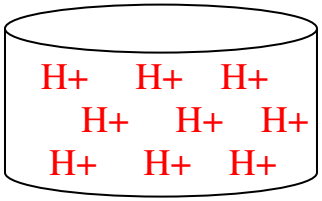
$$HA \rightleftharpoons H^+ + A^- \qquad [H^+] = (K_aC_a)^{0.5}$$

To solve the problem. Trust me, overcome your need to complicate things, and this material gets a lot easier.

Time out 2. A picture of what it means to be a weak acid. If you understand this picture you will be able to understand the derivation of the weak acid expression to follow.

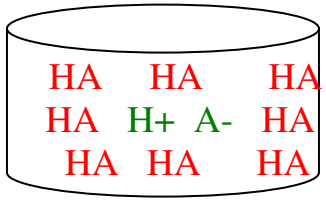
We know that a strong electrolyte when thrown in solution, dissociates completely to form only ion. In the case of a strong acid like HNO3, the container is filled with H+ and NO3-. BUT, NO3- is a spectator ion so the beaker to the right below, which is filled with just a bunch of protons, is representative of the only species in solution that contributes to pH, the H+ concentration.

What matters for a **Strong Acid**



Strong acids: the beaker above
what matters for all 7 strong acids
after the spectator ions are removed

What matters for a **weak acid**



Weak acids: only a few ions dissociate and
most weak acid stays in the form that was added, HA
in other words, weak acids don't react ($\Delta G = -$)

You can see right away why there is such a pH difference between strong and weak acids. Strong acids form only protons making for a low pH. Weak acids barely form any protons, making for a slightly acidic pH.

Time for the weak acid derivation using RICE to yield the weak acid expression: $[H^+] = (K_aC_a)^{0.5}$

We begin with the general case of a weak acid equilibrium

$$HA \rightleftharpoons H^+ + A^- \quad \text{with } K_a = [H^+][A^-]/[HA]$$

and then construct a RICE expression with the following steps:

1. Start with C_a for the amount weak acid HA
2. We assume 0M is the amount of H^+ and A^- to start
3. Since Q< K the reaction shifts right so we add signs to the change array accordingly
4. Assume that x is the concentration of protons that form and will in the chart
5. At equilibrium the concentrations are C_a-x, x and x respectively

Reaction: HA ⇌ H+ + A-

Initial	C_a	0	0
Change	-x	+x	+x
Equilibrium	C_a -x	x	x

Substituting these amounts into the equilibrium expression we get:

$$K_a = [x][x]/[C_a - x]$$

But now we make an important approximation. As mentioned above, by definition, a weak acid doesn't dissociate very much—typical values are maybe one out of a thousand or out of ten thousand. This means that x which is H+ is very small relative to the starting concentration. And in steps:

6. Let the x= $[H^+]$ and then Ka = $[H^+]^2/ (Ca-H^+)$
7. Approximate that H+ is very small because this is a weak acid and it doesn't dissociate so $(C_a - x) \sim Ca$
8. Now simplified, we can rearrange the expression to obtain our famous result for a weak acid:

$$[H^+] = (K_aC_a)^{1/2}$$

What we have done is turn a quadratic equation into a simple weak acid problem we can do in our head by using approximation that weak acids don't dissociate very much (which is true because that is the definition of a weak acid!!) If you want to know the turning point in the derivation, it was when, mathematically we said

$(C_a - x) \sim Ca$ which is what our beaker of weak acid said (all HAs and very little H+)

Time for the weak base derivation using RICE to yield the weak base expression: $[OH^-] = (K_bC_b)^{0.5}$

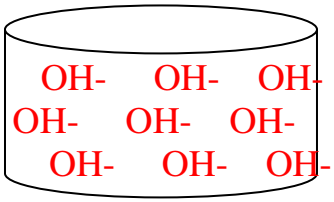
Without wasting the time to show off the derivation, it is not surprising that an analogous equilibrium for weak bases can be derived making the same approximations.

So starting with a neutral weak base like ammonia which we will call B, we can write down

$B \rightleftharpoons BH^+ + OH^-$ $\qquad [OH^-] = (K_bC_b)^{0.5}$

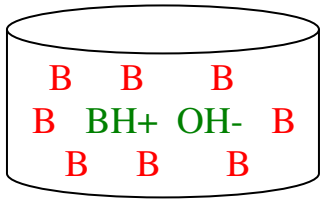
And draw an analogous beaker of weak base to constrast with strong base.

What matters for a **Strong Base**



Strong bases: the beaker above
what matters for all strong bases
after the spectator ions are removed

What matters for a **weak base**



Weak bases: only a few ions dissociate and
most weak base stays in the form that was added, B
in other words, weak bases don't react (ΔG = -)

Try the derivation yourself. The parallels are exactly like the weak acid case. You just need to substitute B for HA, subscript b for a, OH- for H+. You even make the same kind of approximation at the same time. Try it. It is a blast.

Summary of acid base equation types to date with some examples.

Equation 1. Pure water. $[H^+] = K_w^{0.5}$

Example. What is the pH of pure hot water if at a certain temperature if K_w is 1×10^{-13}?

Answer: $[H^+] = K_w^{0.5} = (1 \times 10^{-13)\,0.5} = 10^{-6.5}$ pH = 6.5 (wow, water that isn't pH 7)

Equation 2. Strong acid. $[H^+] = C_a$

Example. What is the pH of 0.01 M chloric acid?

Answer: First note chloric acid is a strong acid. So $[H^+] = C_a = 0.01$ M. pH = 2. Wow, strong acids have a low pH.

Equation 3. Strong base. $[OH^-] = C_b$

Example. What is the pH of 0.01 M cesium hydroxide?

Answer: First note cesium hydroxide is a strong base. So $[OH^-] = C_b = 0.01$ M. pOH = 2. pH = 12. Wow, strong bases have a high pH.

Equation 4. Weak acid. $[H^+] = (K_a C_a)^{1/2}$

Example. What is the pH of 0.01 M formic acid is $K_a = 1 \times 10^{-6}$?

Answer: First note formic acid is not a strong acid so it must be a weak acid.
So $[H^+] = (K_a C_a)^{1/2} = ((.01)(1 \times 10^{-6}))^{0.5} = 1 \times 10^{-4}$ M pH = 4. Wow, weak acids have an intermediate pH between neutrak water and a strong acid.

Equation 5. Weak base. $[OH^-] = (K_bC_b)^{0.5}$

Example. What is the pH of 0.1 M ammonia if $K_b = 1 \times 10^{-5}$?

Answer: First note ammonia is a famous weak base so use the weak base expression.
So $[OH^-] = (K_bC_b)^{0.5} = ((.1)(1 \times 10^{-5}))^{0.5} = 1 \times 10^{-4}$ M pOH = 3. pH = 11. Wow, weak bases have an intermediate pH between neutral water and a strong base.

And that is the extent of acid base calculations for the simplest examples of acid and bases. Sadly, it all gets much harder. The good news. You won't have to take a test on the hard stuff until well after spring break!!