

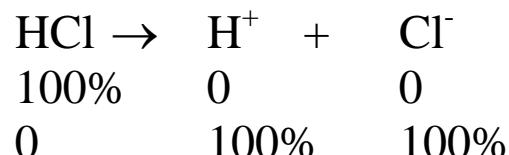
Lecture 16: Polyprotic Acids

We should be pretty comfortable dealing with monoprotic acids like:

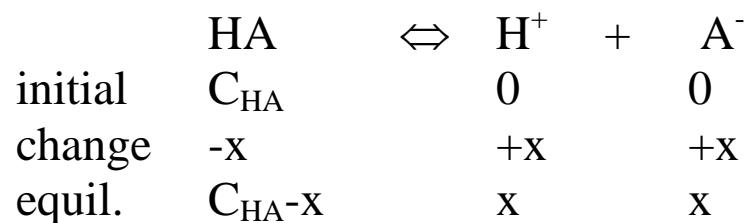


Each of these acids has a single proton to offer to the system. Consequently there is a nice one-to-one stoichiometry to deal with (one mole of acid yields one mole of protons). The chemical equilibria are also usually pretty easy.

You either have the strong acid case:



or the weak acid case:

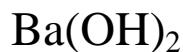


and the calculations can be as simple as

$$[\mathbf{H}^+] = \mathbf{C}_a \quad \text{or} \quad [\mathbf{H}^+] = (\mathbf{K}_a \mathbf{C}_a)^{0.5}$$

But life isn't that easy. 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:

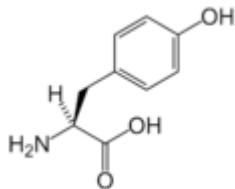
diprotic acids and bases



triprotic acids



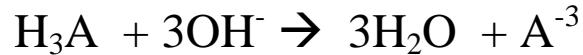
or



tetraprotic acids $(\text{HOOCCH}_2)_2\text{-NCH}_2\text{CH}_2\text{N-(HOOCCH}_2)_2$

Note that in addition to simple inorganic acids and bases, lots of very famous organic molecules (like all the amino acids) or EDTA are polyprotic acids.

Obviously polyprotic systems will be more of a problem to deal with. First the stoichiometry is not a simple one-to-one correspondence. Note the three to one ratio when titrating triprotic acid:



So while not covered here, this is the origin of concepts like equivalence and normality that you might see in the literature and certain textbooks.

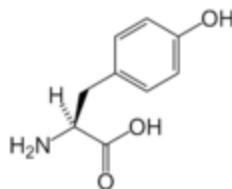
Also, from an equilibrium stand point, we have to recognize that each proton or hydroxide in the molecule had its own acid/base strength which can be defined in terms of its equilibrium constant. Thus if we have a molecule with three protons, there will be three acid base equilibria with their own equilibrium 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 over the molecule. Instead, there will be a first reaction involving the most acidic proton with the resulting conjugate base reacting to yield the next most acidic proton, and so on.

Consider, for example, the following three polyprotic acids:

H_2CO_3 (carbonic acid) a diprotic acid that has two pK values:
 $pK_{a1} = 3.60$ and $pK_{a2} = 10.25$

H_3PO_4 (phosphoric acid) a triprotic acid that has three pK values:
 $pK_{a1}=2.12$, $pK_{a2}=7.21$, and $pK_{a3}=12.67$

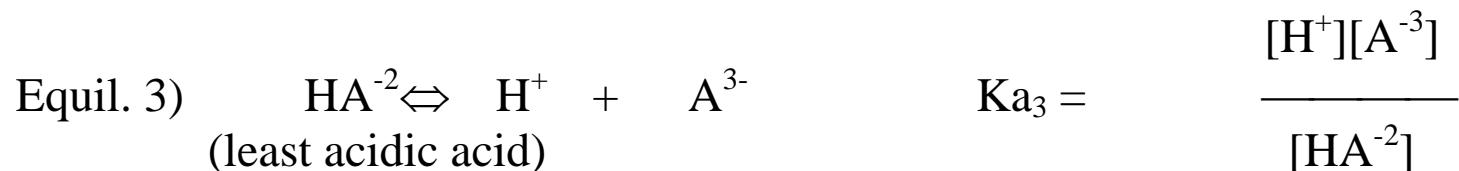
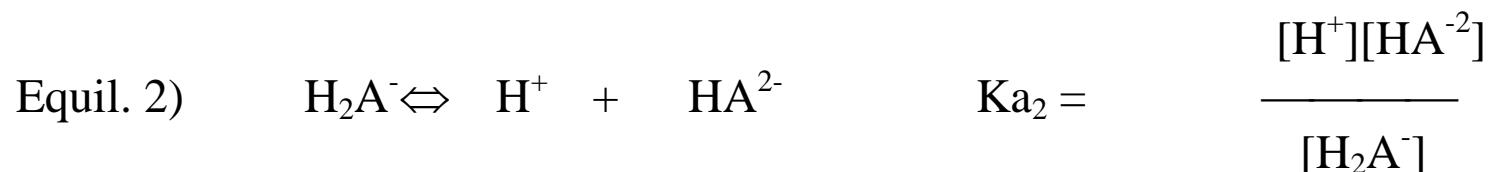
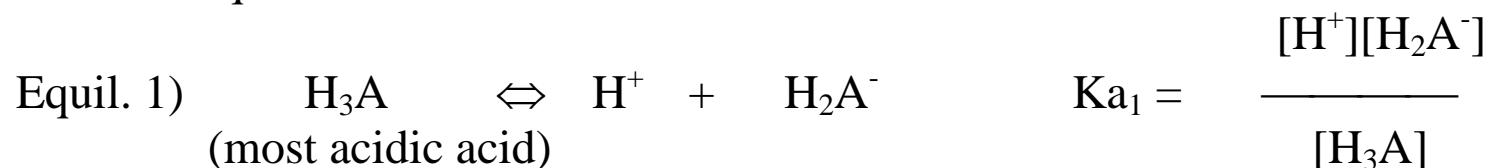


(tyrosine) a triprotic acid that has three pK values:
 $pK_{a1}=2.17$, $pK_{a2}=9.19$, and $pK_{a3}=10.47$

We will examine each of the acids as we construct alpha diagrams and titration curves to represent the important species present as a function of pH. Note, one of these three is not like the others—can you guess?

Writing Equilibrium Expressions for Polyprotic Acids.

Let's write out the equilibrium expressions and equations for the dissociation of a triprotic acid, H_3A . While tedious, it requires little more than what we did to write the equilibrium expression and equation for a monoprotic acid. We just have to do it three times making sure that as we systematically remove a proton, we keep track of our masses and charges on each side of the balanced equation.



Note that we can extend this formalism to any number of equilibria, from carbonic acid, a diprotic case (H_2A) to EDTA, a hexaprotic case (H_6A). As with monoprotic acids, we needn't complicate our calculations by considering what the base is—as long as we have the pK values, we know the relative strength of all the acids and their conjugate bases.

Calculations involving polyprotic acids.

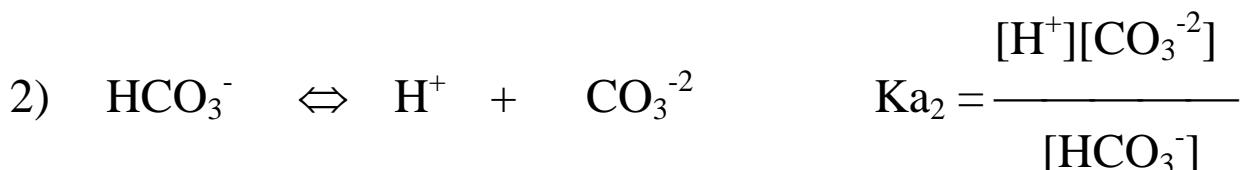
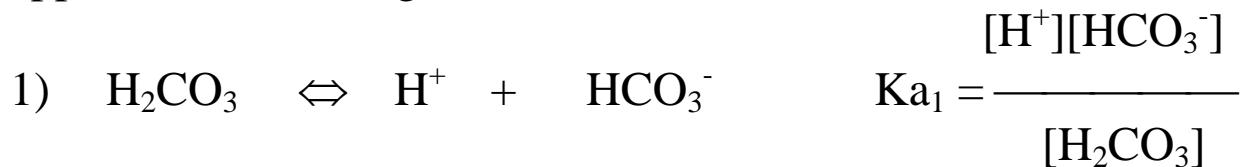
This being an introductory chemistry course, we are usually confronted by polyprotic acids for which the K values are separated by three or four orders of magnitude. As we have learned, when the K values are far apart the calculation of pH becomes greatly simplified because a single equilibrium expression can be used, which means we are dealing with the same monoprotic weak acid and base equations used in a million problems up till now.

Let's see why this happens as we examine the diprotic acid, carbonic acid, H_2CO_3 . Carbonic acid is famous because it is part of the equilibrium describing 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.

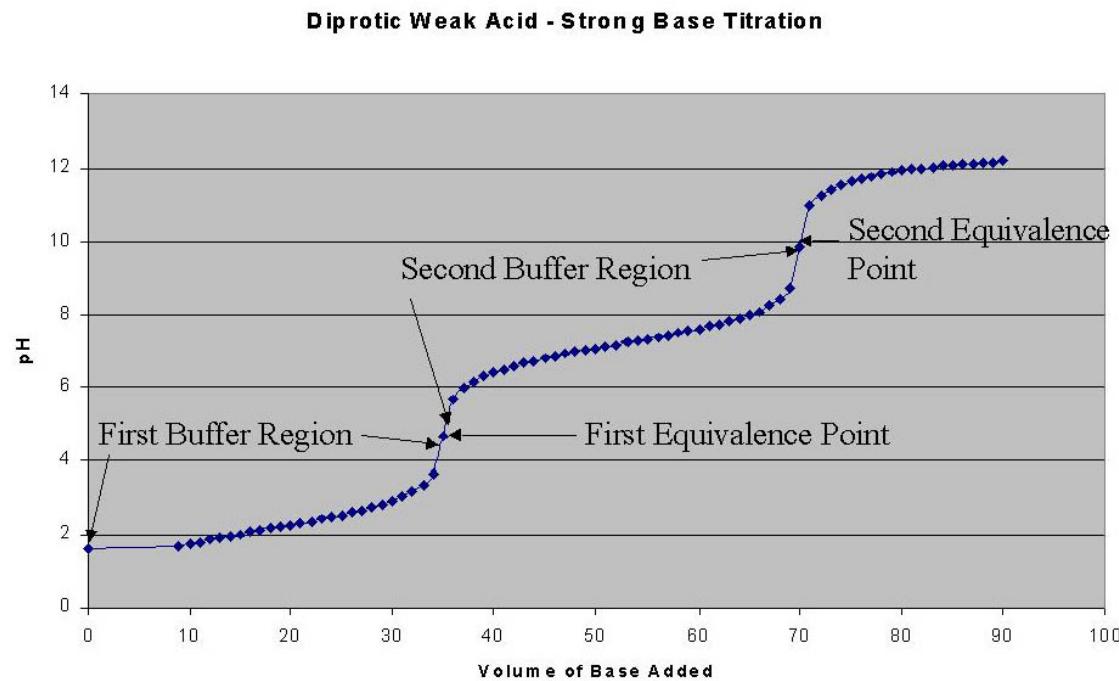
Best of all to general chemistry students, carbonic acid is famous because its K values are six orders of magnitude apart:

$$\text{p}K_{\text{a}1} = 3.60 \text{ and } \text{p}K_{\text{a}2} = 10.25$$

and even spaced perfectly ($\text{p}K_{\text{a}1}$ not too large and $\text{p}K_{\text{a}2}$ not too small) so that we can use the weak acid approximation and ignore K_w .



Recalling the titration curve we created for a weak monoprotic acid, it is easy to see what kinds of calculations you can be asked to do by looking at the curve. A diprotic acid with equilibrium constants spread wide apart will look like someone has glued two monoprotic acid curves together. For example, here is the curve for a diprotic acid like carbonic acid with well-separated K values:



There are six different regions on the curve for which distinctly different calculations are done—note the parallel to the monoprotic acid titration case and you will see that in fact there is only one new kind of calculation to consider:

Case I: Pure weak diprotic acid with H_2CO_3 alone

Case II: The most acidic buffer with H_2CO_3 and HCO_3^-

Case III: The amphiprotic case with HCO_3^- alone—this is the only new calculation

Case IV: The most basic buffer with HCO_3^- and $\text{CO}_3^{=}$

Case V: Pure conjugate base with $\text{CO}_3^{=}$ alone.

Case VI: Excess strong base

Of the six cases, only Case III requires you to learn anything new.

Case I. Calculate the pH of a 0.1 M solution of carbonic acid, H_2CO_3 .

Here we have a single species, a weak acid which has dissolved in solution. We use the K_{a1} equilibrium above which applies to carbonic acid:

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

use simple monoprotic acid
 $[\text{H}^+] = (\text{KaC}_{\text{HA}})^{1/2}$

Case II. Calculate the pH of a solution containing 0.1M H_2CO_3 and NaHCO_3 . Here we have an equation involving carbonic acid and its conjugate base. Hey!! This is a buffer problem involving the first acid equilibrium, K_{a1} .

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$
$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

Case IV. Calculate the pH of a solution containing 0.1M Na_2CO_3 and 0.1 M NaHCO_3 . Looks like another buffer involving HCO_3^- and CO_3^{2-} from the second equilibrium, K_{a2} .

$$\text{pH} = \text{p}K_{a2} + \log \left(C_A^{2-}/C_{\text{HA}}^- \right)$$

$$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Case V. Calculate the pH of a solution containing 0.1 M Na_2CO_3 . Here we have a single species, CO_3^{2-} which is the conjugate base of HCO_3^- . It is found in the second acid equilibrium, K_{a2} , which can be rewritten in terms of CO_3^{2-} as a base and solved as a weak base case:



use weak base case

$$[\text{OH}^-] = (C_B K_B)^{1/2}$$

$$K_b = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

Case VI. Calculate the pH of a solution containing 0.1 M Na_2CO_3 and excess hydroxide. Here we have a weak base dominated by a strong base. The good estimate of the pH is to simply ignore the weak base and use the strong base equation to calculate pH.

$$[\text{OH}^-] = C_b$$

Case III: Amphiprotism in polyprotic acids.

Only one of the six calculations involving a diprotic acid requires that we learn anything new. An examination of the equilibrium expressions reveals that a amphiprotic species occurs N-1 times in a polyprotic acid, where N is the number of protons and happens any time there is a pure compound in solution capable of gaining or losing a proton. For example, in carbonic acid, bicarbonate is amphiprotic, HCO_3^- . In phosphoric acid, there are two amphiprotic species, H_2PO_4^- and HPO_4^{2-} .

What makes the amphiprotic case different is that unlike any other example we have seen, we cannot make an approximation that only one K value matters since obviously a compound capable of gaining or losing a proton needs to include the K value for each reaction.

The good news is that (without showing you all the math) lots of cancelations occur in finding the solution to the amphiprotic acid equation and when everything is done, the equation is simply

$$[\text{H}^+] = (\text{K}_1 \text{K}_2)^{0.5} \quad \text{or} \quad \text{pH} = 0.5 (\text{pK}_1 + \text{pK}_2)$$

In other words, and perhaps not surprisingly, when you have an amphiprotic species, you simply split the difference and the calculation is actually the easiest of any you will do.

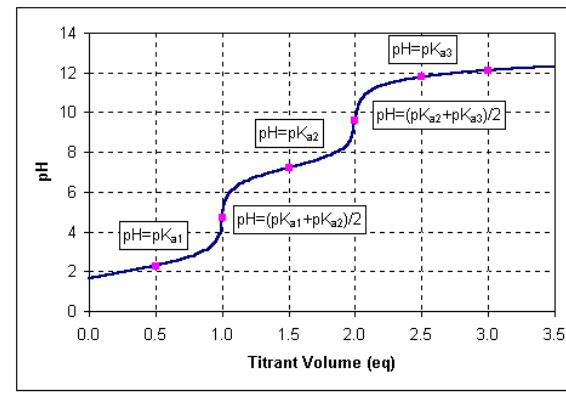
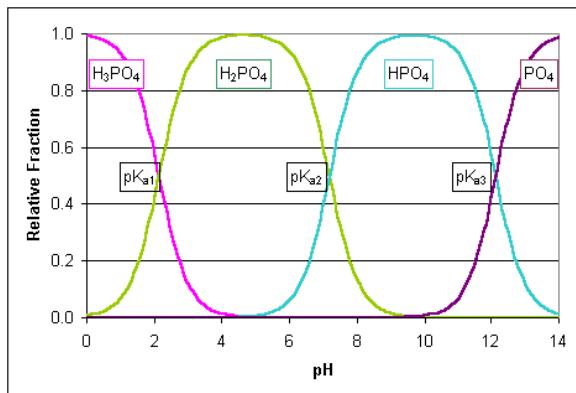
Example: What is the pH of any concentration solution of bicarbonate?

$$\text{pH} = 0.5 (\text{pK}_1 + \text{pK}_2) = 0.5(3.6 + 10.2) = 6.9$$

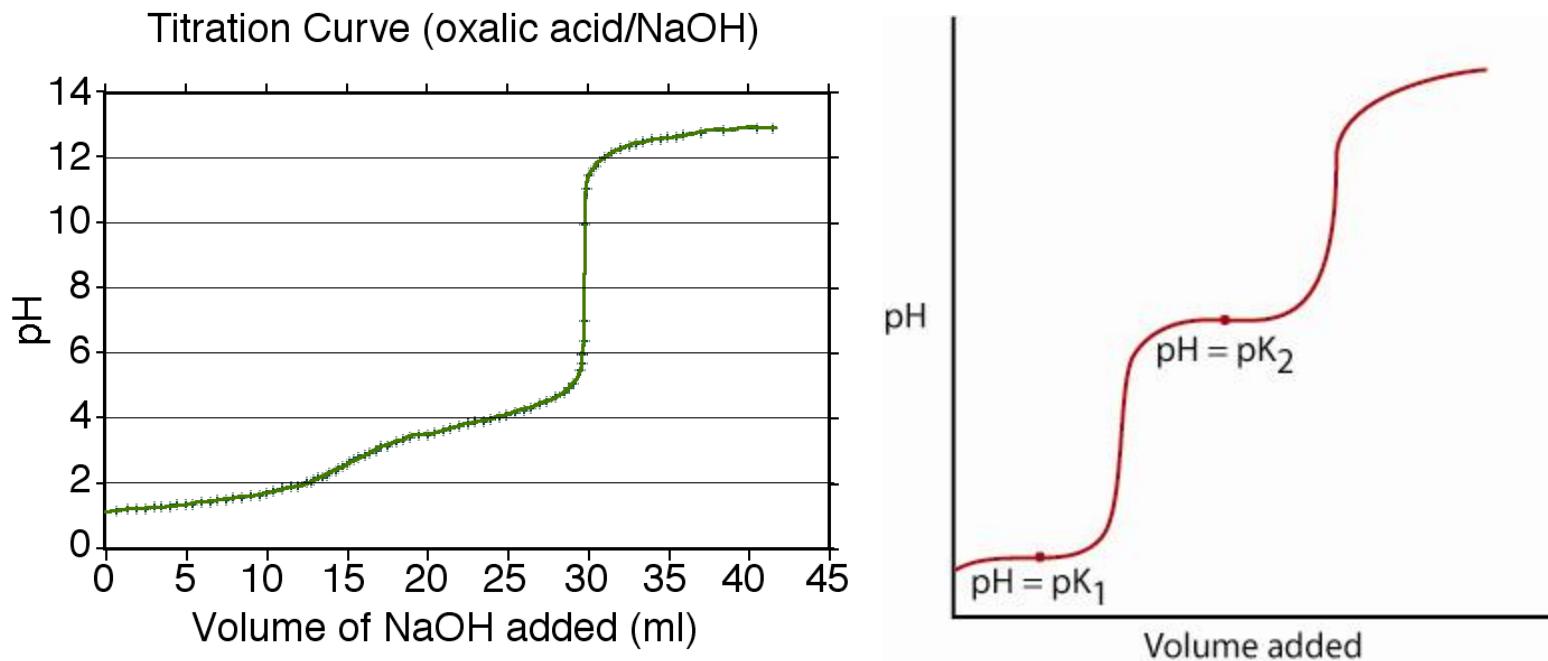
Polyprotic Acids and Reality.

Note that for all of our simplifications to work out, we needed our K values to be far apart in our polyprotic acids. This is one of the reasons we choose to look at carbonic acid and phosphoric acid—aside from being incredibly important in our daily lives, they also permit all the approximations we have learned and allow us to pretend to be doing polyprotic acid calculations when we are actually performing monoprotic acid calculations.

The actuality is that it is rarely the case that Ks are perfectly separated so that we see alpha diagrams and titration curves like those for phosphoric acid below:



Instead, when we go in the lab and perform a titration curve on a polyprotic acid it is far more likely to look like the one of the left for oxalic acid, than the one on the right for carbonic acid.

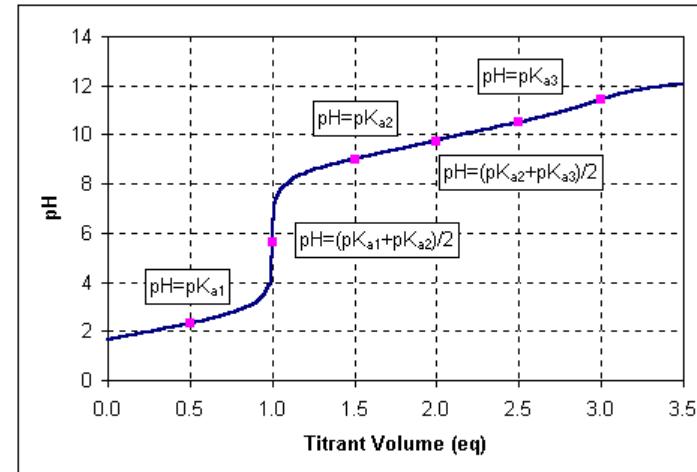
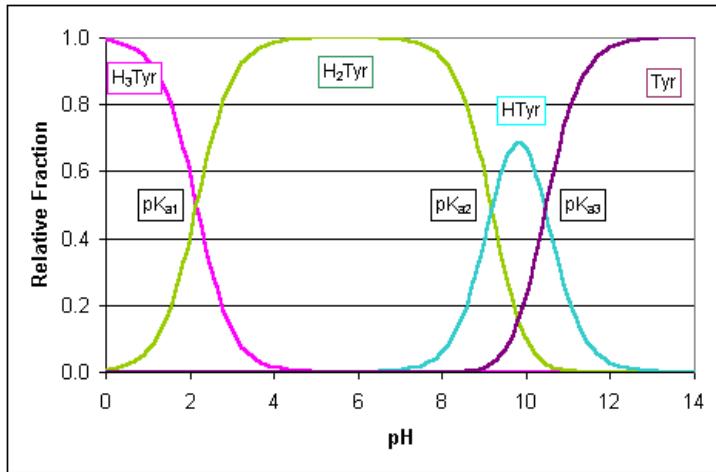


Tyrosine—a “real” polyprotic acid.

Recall at the beginning of this lecture you were given the K values for three different polyprotic acids. If you go back and look at the K values you will see that those for tyrosine are well outside the bounds for a general chemistry class calculation.

$$pK_{a1}=2.17, \quad pK_{a2}=9.19, \quad \text{and} \quad pK_{a3}=10.47$$

Without going into the details, here are what the actual alpha diagrams and titrations curves look like for tyrosine:



Sadly, none of the approximations we used for phosphoric acid would work here. The first dissociation is too acidic and therefore the approximation, $(K_{a1}C_a)^{0.5}$, will have a lot of error. And the second two dissociations corresponding to K_{a2} and K_{a3} are so close together that the inflection points in their equivalence points cannot be discerned. You could hardly expect to treat them as independent weak acids or bases as we did for the carbonic acid and phosphoric acid systems.

Fortunately you have been given the tools for handling these more complicated real-world acids. As you learned in Lecture 15 on complex equilibria, all you need to do is write down as many chemical equilibrium equations and mass and charge balances, as you have unknowns, and you can find the exact solutions without approximation

But we will save that for an advanced course in analytical chemistry.