Chapter 55 ACID-BASE EQUILIBRIA, Part 2

We now turn to calculations involving weak acid equilibria. We've seen such a calculation already: Example 4 in Chapter 52 involved the dissociation of acetic acid. That's very typical of the calculations which you will be doing here. We will now add pH and we will step up our approximation methods. We will also consider acids with more than one dissociation step. Despite these extras, the fundamentals remain the same as done previously. After the calculations, we'll talk a bit about why some acids are strong or weak.

55.1 K_a

Consider a generic weak acid, HA, undergoing dissociation.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium constant K for acid dissociation is specifically designated K_a.

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

Values of K_a have been measured for many acids and these vary widely. Common values are in the range of 10^{-2} to 10^{-10} although some are outside that. As the value of K_a decreases, there is less dissociation and less H^+ at equilibrium, and this constitutes a weaker acid. Conversely, a better acid will be reflected by a larger K_a. A selection of K_a values is given in Appendix B.

A weak acid produces some H^+ in water and this amount of H^+ is in addition to some H^+ which is produced by autoionization. For a typical problem involving a weak acid, we are concerned with the $[H^+]$ and the pH of some solution, so we need to consider both of these sources for total $[H^+]$. Fortunately, autoionization has only a very small impact on total $[H^+]$ in most solutions of acids and bases, and we can therefore ignore it. The reason for this lies in equilibrium dynamics. The autoionization equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

has a very small $K_w = 1.0 \times 10^{-14}$, from which $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M in pure water. Upon adding weak acid, the H^+ from the acid shifts the above equilibrium to the left and that makes autoionization's contribution even smaller. For a quantitative illustration, consider some weak acid at [HA] = 0.010 M and with $K_a = 1.0 \times 10^{-6}$. In this case, the weak acid dissociation by itself provides $[H^+] = 1.0 \times 10^{-4}$ M. If we plug this value for $[H^+]$ into K_w

$$K_w = [H^+]\,[OH^-] = (1.0 \times 10^{-4})\,[OH^-] = 1.0 \times 10^{-14}$$

then we find $[OH^-] = 1.0 \times 10^{-10}$ M. This is a thousand-fold reduction in $[OH^-]$ compared to pure water and this shows the shift to the left for autoionization. Since autoionization gives equal amounts of H^+ and OH^-, then autoionization's contribution to total $[H^+]$ is likewise 1.0×10^{-10} M. The grand total for $[H^+]$ is now the sum of the amounts from acid dissociation and from autoionization.

$[H^+]$ from weak acid dissociation:	0.00010 M
$[H^+]$ from autoionization:	0.00000000010 M
Grand total $[H^+]$:	0.00010 M

The result is that $[H^+]$ from autoionization is not significant to total $[H^+]$ when the acid is present. For our coverage, this will be general and we will ignore the autoionization part completely. Although there are cases close to neutral where autoionization can be significant, we will not deal with those. This discussion also applies to OH^- in the presence of added bases. Thus, when we get to bases, we will ignore autoionization at that time also.

OK, let's start.

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Example 1. The term hydrohalic acid applies to a solution of any of the hydrogen halides dissolved in water. Unlike HCl, HBr and HI which are strong, HF is weak with $K_a = 6.8 \times 10^{-4}$. A solution of HF is prepared by dissolving 0.0448 mol HF in water to make 200. mL of solution. What are the concentrations at equilibrium of HF, H^+ and F^-? What are the pH of the solution and the percent dissociation of HF?

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Except for pH, this is the same type of problem as Example 4 in Chapter 52. Look over that again if you need to get back in the groove.

‣ Step 1. Balanced equation: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

‣ Step 2. K_a

$$K_a = \frac{[H^+]\,[F^-]}{[HF]} = 6.8 \times 10^{-4}$$

‣ Step 3. We need an initial amount and a table to put it in.

$$\text{initial [HF]} = \frac{0.0448 \text{ mol}}{0.200 \text{ L}} = 0.224 \text{ M}$$

	[HF]	[H⁺]	[F⁻]
Initial:	0.224	-0-	-0-

‣ Step 4. Bring in the changes.

	[HF]	[H⁺]	[F⁻]
Initial:	0.224	-0-	-0-
Changes:	$-x$	$+x$	$+x$

‣ Step 5. Final equilibrium amounts.

	[HF]	[H⁺]	[F⁻]
Initial:	0.224	-0-	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.224 - x$	x	x

‣ Step 6. Plug into K_a.

$$K_a = \frac{[H^+]\,[F^-]}{[HF]} = \frac{(x)\,(x)}{0.224 - x} = 6.8 \times 10^{-4}$$

Re-arrange.

$$x^2 + 6.8 \times 10^{-4}\,x - 1.5 \times 10^{-4} = 0$$

Solve for x using the quadratic equation. You will get $x = -0.013$ and 0.012. The negative is the nonsense answer.

‣ Step 7. Take 0.012 back into the equilibrium line of the table for the final concentrations.

$[HF] = (0.224 - 0.012)$ M $= 0.212$ M
$[H^+] = 0.012$ M
$[F^-] = 0.012$ M

‣ Step 8. K-check gives 6.8×10^{-4}, right on.

Time out. We threw this into quadratic but what about approximation? Would this have worked? K_a is getting close to 10^{-3} which is not real small, so this could be iffy. Let's go ahead and try it. Assume we haven't done the quadratic above. Start over at K_a.

$$K_a = \frac{(x)\,(x)}{0.224 - x} = 6.8 \times 10^{-4}$$

If we assume x is small relative to 0.224, then we approximate $0.224 - x \approx 0.224$. That gives us

$$K_a \approx \frac{(x)\,(x)}{0.224} = 6.8 \times 10^{-4}$$

which leads to $x = \pm 0.012$. Only the positive result is valid and it agrees with the value from the quadratic equation, so approximation works here also.

OK, we've got x and we've got the concentrations. We still need a pH and a percent dissociation.

$$\text{pH} = -\log(0.012) = 1.92$$

$$\%\text{diss} = \frac{\text{amount which dissociated}}{\text{starting amount}} \times 100\% = \frac{0.012\ \text{M}}{0.224\ \text{M}} \times 100\% = 5.4\%$$

We're done.

Approximation worked fine in this Example, but I will tell you that it's close to not working. Now we will take our approximation methods up one notch and bring in another consideration. In Chapter 52, we considered the size of K as an indicator of whether approximation might work or not. We will now add concentrations as another indicator. Recall from the Second Principle of Equilibrium Dynamics that dilution favors more Q components. In Chapter 53, we considered this for CH_3CO_2H dissociation.

> ❝ Apply this to the acetic acid equilibrium.
>
> $$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$
>
> If we add water, the immediate effect is to decrease all concentrations and decrease Q. In order to return to equilibrium, $[CH_3CO_2^-]$ and $[H^+]$ will increase while $[CH_3CO_2H]$ will decrease. In the end, more moles of CH_3CO_2H are actually dissociated at the new point of balance. The net result is that the percent dissociation increases upon dilution. This is an extremely important notion in many solution equilibria, as will be seen later in Chapter 55. ❞

Later is now. For all dissociation equilibria, dilution favors more dissociation. Know that. But what's that got to do with approximation? More dissociation means a bigger relative shift and that works against approximation. Thus, dilution can be problematic for approximation. We will illustrate this dilution dilemma by taking Example 1 and diluting it 20-fold.

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Example 2. Repeat Example 1 but with a total solution volume of 4.00 L. What are the concentrations at equilibrium of HF, H^+ and F^-? What are the pH of the solution and the percent dissociation of HF?

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The setup is the same but some numbers are different. The balanced equation and K_a are the same.

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

$$K_a = \frac{[H^+]\,[F^-]}{[HF]} = 6.8 \times 10^{-4}$$

You need a new initial

$$\text{initial [HF]} = \frac{0.0448\ \text{mol}}{4.00\ \text{L}} = 0.0112\ \text{M}$$

and a few changes in the table.

	[HF]	$[H^+]$	$[F^-]$
Initial:	0.0112	-0-	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.0112 - x$	x	x

Plug into K_a.

$$K_a = \frac{[H^+]\,[F^-]}{[HF]} = \frac{(x)\,(x)}{0.0112 - x} = 6.8 \times 10^{-4}$$

Re-arrange.

$$x^2 + 6.8 \times 10^{-4}\,x - 7.6 \times 10^{-6} = 0$$

The quadratic equation will give $x = -0.0031$ and 0.0024. The negative is again nonsense. Put 0.0024 into the last line of the table for x.

$[HF] = (0.0112 - 0.0024)\ \text{M} = 0.0088\ \text{M}$
$[H^+] = 0.0024\ \text{M}$

$[F^-] = 0.0024$ M

You can do the K-check. It's close enough.

Now we pause to bring in approximation for comparison. Again, assume we don't know the answers from the quadratic solution. Let's again go back to K_a.

$$K_a = \frac{(x)\,(x)}{0.0112 - x} = 6.8 \times 10^{-4}$$

Assume x is small relative to 0.0112; thus, $0.0112 - x \approx 0.0112$.

$$K_a \approx \frac{(x)\,(x)}{0.0112} = 6.8 \times 10^{-4}$$

Solving for x will now give ±0.0028 and the negative is again nonsense. Unfortunately, the positive 0.0028 is now a bit different from the answer by the quadratic route, so the present answer is not good enough. Approximation does not work well here. Too bad.

Let's finish off this Example using 0.0024 from the quadratic result. The pH is

$$\text{pH} = -\log(0.0024) = 2.62$$

and the percent dissociation is

$$\%\text{diss} = \frac{\text{amount which dissociated}}{\text{starting amount}} \times 100\% = \frac{0.0024\text{ M}}{0.0112\text{ M}} \times 100\% = 21\%$$

and that wraps up the final answers.

Note the 21% dissociation. That's what killed simple approximation here. That 21% is way too much of a relative change. In Example 1, the relative change was only 5.4% and approximation worked. The K_a value was the same for both Examples, so this illustrates that a K by itself is not the only indicator to consider. We now refine our approach as follows. For dissociation equilibria, approximation works best for smaller K and/or higher concentrations. Both of these factors give less relative change (smaller %diss) from initial conditions. Note also the converse. When K is moderate (not so small) and/or when concentrations are more dilute, then approximation is more prone to fail.

So does that mean the 0.0028 answer from simple approximation is totally wrong? That's up to your instructor. That's not the end of approximation, however, because there is another refinement available called iteration.

55.2 Iterate, iterate, iterate

The term "iterate" follows the normal dictionary meaning which is to repeat. Iteration involves repeat approximation. There are four steps to iteration but the first is not new.

Iteration

A. Do the simple approximation for x.
B. Plug this answer into <u>the quantity which was approximated</u>.
C. Solve for a new x.
D. Repeat Steps B and C until consecutive answers agree to the correct sigfigs (or cycle within the last sigfig, although this is less common).

For Step B, the underlined phrase is important. For Step D, the parenthetical part will be illustrated in Example 3.

Let's illustrate iteration using Example 2. Upstairs, we did the usual, simple approximation

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112} = 6.8 \times 10^{-4}$$

which gave $x = 0.0028$. That ends Step A of iteration. For Step B, we plug this value for x back into the quantity which we had approximated. We only approximated the denominator; we did not approximate the numerator. Thus, we plug in 0.0028 for x in the denominator only.

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112 - 0.0028} = \frac{x^2}{0.0084} = 6.8 \times 10^{-4}$$

For Step C, solve again for x: you get 0.0024. That's quite different from 0.0028. Are we done? Step D says do Steps B and C again.

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112 - 0.0024} = \frac{x^2}{0.0088} = 6.8 \times 10^{-4}$$

Solving gives $x = 0.0024$ which is the same as the prior result. Now Step D says stop. This is your final answer for x. Notice that it matches the value from the full quadratic solution done previously. Iteration worked.

So what? The full quadratic worked also. Why do we need iteration?

Good question. It's another tool, and it's a very good tool in a range of applications. Iteration methodologies can get very sophisticated; they play a critically important role in many computational methods, in which case the repetitive part is run by software. Those programs can run iterations through hundreds or thousands or more cycles. While our use here is not that sophisticated, you can still get a feel for the method. For our types of problems, iteration does three things. First, it provides a check on the usual approximation. Thus, if you are in doubt whether simple approximation is good enough for a particular problem, then iteration will tell you. Second, iteration gives more leeway to the range of K's and concentrations which can be done, as demonstrated by its success in handling Example 2 when simple approximation was not enough. Third, not all problems can be solved directly and some form of approximation will be necessary in those cases.

Although it is better than simple approximation and it gives more leeway, iteration is still an approximation method and it should not be used where it doesn't belong. There are two clues to the failure of iteration for a particular problem which you should be aware of.

- Successive iterations give numbers for x which jump around a lot and do not show a clear direction.
- Successive iterations still do not agree after 10 or 12 or more cycles.

If either of these is happening, then iteration was not the correct tool for the job. (Or you made a math error somewhere, which can happen with any method.)

In our current usage for a weak acid dissociation problem, you now have two tools to choose from. You can solve directly by way of quadratic equation or you can solve by approximation/iteration. The two methods usually give the same answer although sometimes they can differ by one in the last sigfig. That's no big deal and either answer would be acceptable. Besides, we are sort of taking it easy on the quadratic equation anyway with our simplified sigfig rule. So, use either way; it's your call. Of course, if your instructor wants them done a certain way, then call it that way. But if you have the choice, then you need to decide which way is faster and more reliable for you. Try them both and find out. Here: compare the two methods for Example 2 starting from the K_a expression.

$$K_a = \frac{(x)\,(x)}{0.0112 - x} = 6.8 \times 10^{-4}$$

For direct (quadratic) method, you had to get from there to

$$x^2 + 6.8 \times 10^{-4}\,x - 7.6 \times 10^{-6} = 0$$

and then into

$$x = \frac{-(6.8 \times 10^{-4}) \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(1)(-7.6 \times 10^{-6})}}{2(1)}$$

in order to get x. For the iteration method, you worked with the K_a expression directly and you had to execute three cycles.

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112} = 6.8 \times 10^{-4} \quad \rightarrow\rightarrow\rightarrow \quad x = 0.0028$$

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112 - 0.0028} = \frac{x^2}{0.0084} = 6.8 \times 10^{-4} \quad \rightarrow\rightarrow\rightarrow \quad x = 0.0024$$

$$K_a = \frac{x^2}{0.0112 - x} \approx \frac{x^2}{0.0112 - 0.0024} = \frac{x^2}{0.0088} = 6.8 \times 10^{-4} \quad \rightarrow\rightarrow\rightarrow \quad x = 0.0024$$

Three cycles are not a lot, but some problems will run more. It just depends. So, overall, which method would you prefer? Some students can rip through an algebraic re-arrangement and quadratic solution in no time. Other students are more prone to errors in the middle steps of the derivation and tend to shy away from it. On the other hand, iteration can be tedious, especially if a lot of cycles are involved. You have to try both ways. Another plus for iteration is that it can help in other types of problems in chemistry and also in other fields.

Here's another Example and a quirk. The quirk relates to the parenthetical part of Iteration Step D above.

Example 3. 0.00820 mol HNO_2 was dissolved in a solution of total volume 200.0 mL. What are $[H^+]$ and the pH? K_a for nitrous acid is 7.1×10^{-4}.

- Step 1. Balanced equation: $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$
- Step 2. K_a

$$K_a = \frac{[H^+]\,[NO_2^-]}{[HNO_2]} = 7.1 \times 10^{-4}$$

- Step 3. Initial amount and a table.

$$\text{initial } [HNO_2] = \frac{0.00820 \text{ mol}}{0.200 \text{ L}} = 0.0410 \text{ M}$$

	$[HNO_2]$	$[H^+]$	$[NO_2^-]$
Initial:	0.0410	-0-	-0-

- Step 4. Changes.

	$[HNO_2]$	$[H^+]$	$[NO_2^-]$
Initial:	0.0410	-0-	-0-
Changes:	$-x$	$+x$	$+x$

- Step 5. Final equilibrium amounts.

	$[HNO_2]$	$[H^+]$	$[NO_2^-]$
Initial:	0.0410	-0-	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.0410 - x$	x	x

- Step 6. Plug into K_a.

$$K_a = \frac{[H^+]\,[NO_2^-]}{[HNO_2]} = \frac{(x)\,(x)}{0.0410 - x} = 7.1 \times 10^{-4}$$

Solve for x. We'll first do the quadratic route. Re-arrange.

$$x^2 + 7.1 \times 10^{-4}\,x - 2.9 \times 10^{-5} = 0$$

You will get $x = 0.0050$ as the usable answer.

Now solve for x using iteration. For this, approximate the final equilibrium value for $[HNO_2]$ as $0.0410 - x \approx 0.0410$.

$$K_a = \frac{x^2}{0.0410 - x} \approx \frac{x^2}{0.0410} = 7.1 \times 10^{-4}$$

Solving for x gives $x = 0.0054$. Iterate.

$$K_a = \frac{x^2}{0.0410 - x} \approx \frac{x^2}{0.0410 - 0.0054} = \frac{x^2}{0.0356} = 7.1 \times 10^{-4}$$

This gives $x = 0.0050$. Iterate again.

$$K_a = \frac{x^2}{0.0410 - x} \approx \frac{x^2}{0.0410 - 0.0050} = \frac{x^2}{0.0360} = 7.1 \times 10^{-4}$$

$x = 0.0051$. Go again.

$$K_a = \frac{x^2}{0.0410 - x} \approx \frac{x^2}{0.0410 - 0.0051} = \frac{x^2}{0.0359} = 7.1 \times 10^{-4}$$

You again get $x = 0.0050$, which was the same value as two x's ago. If you iterate that, you will get 0.0051, and these two numbers just cycle back and forth with each iteration. This is somewhat of a quirk and it ties into how we are dealing with the sigfigs. This is not a very common outcome. If it does happen to you on some problem, just stop when you repeat a prior number and average the two repeating numbers together. Here, averaging 0.0050 and 0.0051 gives 0.0050 to the correct sigfigs. This does match the value from the quadratic route but a difference of 0.0001 would have been OK anyway. Now wrap it up.

‣ Step 7. We have $x = 0.0050$ and this is the molarity for $[H^+]$. This gives pH = 2.30.

Your turn. By the way, from now on, if the K_a is not given in the problem, check Appendix B.

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Example 4. 0.0181 mol of hypochlorous acid is dissolved in 500. mL solution. What are the concentrations at equilibrium of HClO, H^+ and ClO^-? What are the pH and the percent dissociation?

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Balanced equation:

K_a expression:

Initial amount:

Fill in a table:

	[HClO]	$[H^+]$	$[ClO^-]$
Initial:			
Changes:			
Equilibrium:			

Plug into K_a.

How do you want to solve for x? Take your pick. Better yet, do them both.

Quadratic:

Approximation/iteration:

Once you've got x, you can do the concentrations.

$[HClO]$ =

$[H^+]$ =

$[ClO^-]$ =

You can do your K-check.

If that's OK, do the pH,

and, finally, do the percent dissociation.

As one check for your answers, the pH is 4.48. The very small percent dissociation made it very straightforward for approximation/iteration.

These Examples 1 - 4 show the typical calculations and methods which are involved in many acid dissociation problems. Of course, variations are possible. Here's one.

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Example 5. Phenol, C_6H_5OH, was mentioned back in Section 36.1 for sublimation, smell, and antiseptic applications. In water it is a weak acid, and historically it was known as carbolic acid. 0.0136 mol of phenol is dissolved in 100. mL solution. The pH at equilibrium is measured to be 5.43. Find K_a, pK_a and $\Delta G°$ for the dissociation of phenol at 25 °C.

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This starts out a bit different and it asks for different things. Go ahead and set up a balanced equation and a K_a expression.

$$C_6H_5OH(aq) \rightleftharpoons H^+(aq) + C_6H_5O^-(aq)$$

$$K_a = \frac{[H^+]\,[C_6H_5O^-]}{[C_6H_5OH]}$$

and then initialize your acid.

$$\text{initial } [C_6H_5OH] = 0.136 \text{ M}$$

Now what?

For this Example, you must find the value for K_a. (It's not in Appendix B.) That will then lead to pK_a and $\Delta G°$. We could find K_a if we have some numbers to plug in for equilibrium concentrations, but we have an initial (not equilibrium) acid concentration. Note that the pH was given <u>at</u> equilibrium, so we can get the equilibrium amount of $[H^+]$ from the pH. Since it's at equilibrium, this is not a change problem and we don't need a change table.

$$[H^+] = 10^{-5.43} \text{ M} = 3.7 \times 10^{-6} \text{ M}$$

The dissociation gives H^+ and $C_6H_5O^-$ in equal amounts.

$$[H^+] = 3.7 \times 10^{-6} \text{ M} = [C_6H_5O^-]$$

The equilibrium amount of $[C_6H_5OH]$ is the initial amount minus the amount which has dissociated.

$$[C_6H_5OH] = 0.136 \text{ M} - 3.7 \times 10^{-6} \text{ M} = 0.136 \text{ M}$$

Now you've got everything for K_a.

$$K_a = \frac{[H^+]\,[C_6H_5O^-]}{[C_6H_5OH]} = \frac{(3.7 \times 10^{-6})(3.7 \times 10^{-6})}{0.136} = 1.0 \times 10^{-10}$$

There's the K_a. Now p that.

$$pK_a = -\log(1.0 \times 10^{-10}) = 10.00$$

Finally, $\Delta G°$.

$$\Delta G° \;=\; -RT\ln K_a \;=\; -(8.314\text{ J/K})(298\text{ K})\ln(1.0\times10^{-10}) \;=\; 57\text{ kJ}$$

The value is positive and the process is endergonic, as to be expected for a weak acid. Notice the common log in one calculation and natural ln in the other. Don't confuse them.

55.3 Mono vs. poly

Let's now dissociate a bit more.

All calculations with weak acids so far have involved monoprotic acids. A monoprotic acid is an acid which is capable of losing one H^+. Acids which can lose more than one H^+ are called polyprotic acids. Within that category, these can be further specified by the number of H^+ which can be lost. For example, a diprotic acid can lose two H^+ and a triprotic can lose three. H_2SO_4 is the most common example of a diprotic while H_3PO_4 is the most common example of a triprotic. Other examples of diprotics are H_2CO_3 and $H_2C_2O_4$, while another triprotic is given by citric acid, $C_3H_5O(CO_2H)_3$, of citrus fruit fame. Some acids can lose four or more H^+ and the terms do go higher than triprotic, but those are much less common.

Polyprotic acids often undergo dissociation one step at a time and each step is an equilibrium. Each step takes a number, and the first dissociation begins with the starting, neutral acid. Here is an illustration of the two steps for oxalic acid.

First dissociation step $\quad H_2C_2O_4(aq) \rightleftharpoons H^+(aq) + HC_2O_4^-(aq)$

$$K_{a1} \;=\; \frac{[H^+]\,[HC_2O_4^-]}{[H_2C_2O_4]} \;=\; 0.054$$

Second dissociation step $\quad HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq)$

$$K_{a2} \;=\; \frac{[H^+]\,[C_2O_4^{2-}]}{[HC_2O_4^-]} \;=\; 5.4\times10^{-5}$$

Note the inclusion of subscript numbers within the K_a's to indicate the step number. You need to be careful with step numbers. Whenever a number for a dissociation is given, then it traces back to starting, neutral acid; the dissociation of the starting, neutral acid is the first step. You don't always have to work with step numbers, however, as long as you are careful with the meaning. For example, we can independently consider the dissociation of $HC_2O_4^-$ by itself

$$HC_2O_4^-(aq) \rightleftharpoons H^+(aq) + C_2O_4^{2-}(aq)$$

and the K_a for this equation is the K_a for $HC_2O_4^-$. This equation is the same as the second dissociation of $H_2C_2O_4$. Thus, "K_a for $HC_2O_4^-$" is the same as saying "K_{a2} for $H_2C_2O_4$". Watch the wording.

Carbonic acid, H_2CO_3, is also diprotic but this one is not straightforward. H_2CO_3 has only a feeble existence in aqueous solution. This was first noted back in Section 11.3, and we can now elaborate more upon the equilibria involved. When $CO_2(g)$ dissolves in water, some $H_2CO_3(aq)$ is produced but the reality is that very little H_2CO_3 is present at equilibrium; most of the solute is simply $CO_2(aq)$. Carbonic acid can be made as a pure compound but, in water, it decomposes to $CO_2(aq)$ and $H_2O(l)$.

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$

$$K(\text{decomp}) \;=\; \frac{[CO_2]}{[H_2CO_2]}$$

It has been difficult to measure K(decomp) precisely, and values in the range of 380 - 800 have been reported. Nevertheless, the bottom line is that dissolved CO_2 is mostly $CO_2(aq)$, and less than 0.3% is H_2CO_3. The primary equilibria for acid dissociation are therefore based on $CO_2(aq)$.

First dissociation step $\quad CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$$K_{a1} \;=\; \frac{[H^+]\,[HCO_3^-]}{[CO_2]} \;=\; 4.5\times10^{-7}$$

Second dissociation step $\quad HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

$$K_{a2} \;=\; \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} \;=\; 4.7\times10^{-11}$$

Although the amount of CO_2 greatly exceeds the amount of H_2CO_3, you can still consider the dissociation of H_2CO_3 directly. This will likewise be two steps. The first step looks typical and the second step is the same as above.

First dissociation step $\quad H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$$K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$$

Second dissociation step $\quad HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

$$K_{a2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

The value of K_{a1} for H_2CO_3 is also difficult to measure. It is actually related to K(decomp) by summation of the following equilibria.

$$\begin{array}{ll} K(\text{decomp}) & H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l) \\ K_{a1}(CO_2) & \underline{CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \\ K_{a1}(H_2CO_3) & H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \end{array}$$

Since we are summing equations, we multiply K's.

$$K(\text{decomp}) \times K_{a1}(CO_2) = K_{a1}(H_2CO_3)$$

K_{a1} for CO_2 is known very well (4.5×10^{-7}), but the others are not. From the range above for K(decomp), you can calculate $K_{a1}(H_2CO_3)$ to be in the range of 1.7×10^{-4} - 3.6×10^{-4}. Due to the difficulty of measuring K(decomp) and $K_{a1}(H_2CO_3)$, calculations for these solutions are simply based on CO_2 and its K_{a1}.

SO_2 was also noted back in Section 11.3 for similarities to CO_2 but there are also some differences. SO_2 was thought for many years to dissolve in water to produce sulfurous acid, H_2SO_3, but that appears to be wrong. Unlike H_2CO_3 which does have some minor existence in water, there is no H_2SO_3 to any measurable extent. In fact, H_2SO_3 has never even been prepared in pure form under any condition. Thus, "$H_2SO_3(aq)$" really means $SO_2(aq)$ and $H_2O(l)$. The weak acid steps are the following.

First dissociation step $\quad SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$

$$K_{a1} = \frac{[H^+]\,[HSO_3^-]}{[SO_2]} = 0.014$$

Second dissociation step $\quad HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq)$

$$K_{a2} = \frac{[H^+]\,[SO_3^{2-}]}{[HSO_3^-]} = 6.7 \times 10^{-8}$$

Since there is no H_2SO_3 in water, then these are the only equilibria to consider.

The cases of $CO_2(aq)$ and $SO_2(aq)$ are different from other acids but that alone would not warrant their mention here. What does warrant their mention is their tremendous importance on a huge scale. For example, CO_2 and SO_2 are immensely important in the chemistry of Earth's atmosphere, as gases and as solutes in air-borne water droplets. Both contribute in a big way to acid rain. Although there is far more CO_2 in the atmosphere, SO_2 has a much greater K_{a1}. Furthermore, SO_2 is oxidized in the atmosphere and eventually converted to the strong acid, H_2SO_4. Besides pH effects, CO_2 is also a major greenhouse gas which further adds to its atmospheric importance. But the impact of CO_2 is not just up in the air. CO_2 is of major physiological importance to humans (and to plants and to other animals) as a major combustion product of life. The bodily interplay of $CO_2(g)$, $CO_2(aq)$, $H_2CO_3(aq)$ and $HCO_3^-(aq)$ at physiological pH are all vastly important. (Although CO_3^{2-} is the end ion of the dissociations, its concentration is not significant at physiological pH.) The aqueous equilibria above play a role in these various processes, as does the solubility equilibrium for $CO_2(g)$ which we have considered at various places in prior Chapters.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

There's no escaping it: these things are part of your world. You could even go back to Example 6 in Chapter 47 and calculate the pH for the carbonated water in that Example. (It's 3.62, but you ought to look at the next Example in this Chapter before you try that.)

By the way, as a practical matter, the peculiarities of CO_2 and SO_2 do not change a typical K_a or pH calculation. You just treat the acidity of CO_2 and of SO_2 as you would any other weak acid, given some initial amounts for CO_2 or SO_2. We'll cover a CO_2 problem in Example 6 below but let me finish off a few other points first.

The dissociations so far are for diprotic acids. Let's now take a look at a triprotic, H_3PO_4.

First dissociation step $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$

$$K_{a1} = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]} = 7.1 \times 10^{-3}$$

Second dissociation step $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

$$K_{a2} = \frac{[H^+]\,[HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3 \times 10^{-8}$$

Third dissociation step $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

$$K_{a3} = \frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

As always, for each step of dissociation, you lose one H^+. Also, keep in mind the part about step numbers. For example, note that K_a for HPO_4^{2-} is the same as K_{a3} of H_3PO_4.

In the polyprotic examples cited so far, $HC_2O_4^-$, HCO_3^-, HSO_3^-, $H_2PO_4^-$ and HPO_4^{2-} are all hydrogen anions. All hydrogen anions derive from polyprotic acids and all are middle members of the polyprotic series. So far, all of these hydrogen anions are amphoteric.

Let's now consider H_2SO_4. This is different from most polyprotics because its first dissociation is strong. Although the first step is strong, its second dissociation is weak.

First dissociation $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$

Second dissociation $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

$$K_{a2} = \frac{[H^+]\,[SO_4^{2-}]}{[HSO_4^-]} = 0.010$$

K_{a1} is not shown because K_a's are usually not well known for strongs. The first dissociation is strong because HSO_4^- is not pulling back on H^+ to a significant extent. Since it is not pulling back, HSO_4^- is not basic. Since it is not basic, HSO_4^- is not amphoteric; it is only acidic. This will be general:

All hydrogen anions from strong acids are acidic but not amphoteric.

This connects to your flag in Section 54.4. Remember overall that hydrogen anions can be amphoteric or (only) acidic.

Let's start in on some calculations.

Multiple dissociation steps can cause difficulty in calculations involving polyprotics. Since each step can produce some H^+, the question arises as to whether we need to worry about all of the dissociation steps for total $[H^+]$. The answer is: it depends.

For polyprotics whose first step is strong, then the calculation for total H^+ must involve both the strong first step and the weak second step. We will see this for H_2SO_4 in Example 7. For polyprotic acids with all weak steps, then the calculation for total H^+ can get ugly. To avoid utter ugliness, we impose a simplification: we limit coverage to calculations where the amount of H^+ is only significant from the immediate first step. I'll explain this better as we go through the next Example.

. . . .

Example 6. 0.00203 mol CO_2 is dissolved in water to make 1.00 L of solution. What are the concentrations of CO_2, H^+ and HCO_3^- at equilibrium? What is the pH of the solution?

. . . .

Consider again the two dissociation steps.

First dissociation $CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ $K_{a1} = 4.5 \times 10^{-7}$

Second dissociation $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = 4.7 \times 10^{-11}$

Note that the problem asks for concentrations of CO_2, H^+ and HCO_3^-. All of these are directly involved in the first step. H^+ and HCO_3^- are also involved in the second step, but we will wait on that momentarily and do the first step first.

$$K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} = 4.5 \times 10^{-7}$$

Initial $[CO_2]$ is 0.00203 M. Now, set up a table.

	$[CO_2]$	$[H^+]$	$[HCO_3^-]$
Initial:	0.00203	-0-	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.00203 - x$	x	x

Plug in.

$$K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} = \frac{(x)\,(x)}{0.00203 - x} = 4.5 \times 10^{-7}$$

How do you wish to solve? K_{a1} is very small which is good for approximation, but the sample is very dilute. Approximation/iteration? Quadratic? All of the above? Sure, why not?

First, assume $0.00203 - x \approx 0.00203$.

$$K_{a1} = \frac{(x)\,(x)}{0.00203 - x} \approx \frac{x^2}{0.00203} = 4.5 \times 10^{-7}$$

This gives $x = 3.0 \times 10^{-5}$. So far, that is simple approximation. How good an answer is this? Iterate.

$$K_{a1} \approx \frac{(x)\,(x)}{0.00203 - 0.000030} = \frac{x^2}{0.00200} = 4.5 \times 10^{-7}$$

You will again get $x = 3.0 \times 10^{-5}$. Stop.

For the quadratic method, start from K_{a1}

$$K_{a1} = \frac{(x)\,(x)}{0.00203 - x} = 4.5 \times 10^{-7}$$

and re-arrange to

$$x^2 + 4.5 \times 10^{-7}\,x - 9.1 \times 10^{-10} = 0$$

and plug into quadratic to get $x = 3.0 \times 10^{-5}$, same as above.

This gives our answers for first dissociation.

$[CO_2] = (0.00203 - 3.0 \times 10^{-5})\text{ M} = 0.00200\text{ M}$
$[H^+] = [HCO_3^-] = 3.0 \times 10^{-5}\text{ M}$
$\text{pH} = -\log(3.0 \times 10^{-5}) = 4.52$

Now, what about the second dissociation?

Although additional H^+ is produced in the second dissociation, the self-imposed simplification says that the additional amount is not significant compared to the amount from the first step. Ergo, we're done. The second step will also affect the amount of HCO_3^-, but that effect will likewise not be significant to the first step. Thus, we work only with the amounts of H^+ and HCO_3^- from the first step. This approach is valid whenever the value of K_{a2} is very small compared to the value of $[H^+]$ from the first step, which is certainly the case in this Example.

OK, so we've got $[CO_2]$, $[H^+]$ and $[HCO_3^-]$ as requested for this Example, but what if we also needed to find $[CO_3^{2-}]$? CO_3^{2-} is not in the first step. If you need to find the concentration for carbonate, then you have no choice but to invoke the second step. We will now extend this Example to ask this very question: for the solution as given, what is the concentration of CO_3^{2-} at equilibrium?

Bring in the second step.

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

$$K_{a2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

You will solve for $[CO_3^{2-}]$ in the usual way. First, we need initial $[HCO_3^-]$. The initial amounts for the second step pick up where the first step left off. Thus, initial $[HCO_3^-] = 3.0 \times 10^{-5}$ M. We also have some initial $[H^+]$ going into the second step. Set up a table and spell everything out. I'll use *y*'s here to avoid confusion with *x*'s in the prior table.

	$[HCO_3^-]$	$[H^+]$	$[CO_3^{2-}]$
Initial:	3.0×10^{-5}	3.0×10^{-5}	-0-
Changes:	$-y$	$+y$	$+y$
Equilibrium:	$3.0 \times 10^{-5} - y$	$3.0 \times 10^{-5} + y$	y

Plug in.

$$K_{a2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{(3.0 \times 10^{-5} + y)\,(y)}{3.0 \times 10^{-5} - y} = 4.7 \times 10^{-11}$$

This equation is more complicated than usual. Approximate? The HCO_3^- is very dilute at 3.0×10^{-5}, but K_{a2} is 10^{-11}. With such an extremely small K_a, assume y is small relative to 3.0×10^{-5}; this assumption applies for both the numerator and the denominator.

$$K_{a2} = \frac{(3.0 \times 10^{-5} + y)\,(y)}{3.0 \times 10^{-5} - y} \approx \frac{(3.0 \times 10^{-5})\,(y)}{3.0 \times 10^{-5}} = 4.7 \times 10^{-11}$$

This gives $y = 4.7 \times 10^{-11}$. So far, that's simple approximation. What do you think? Is that a good enough answer? What would happen if you iterate? Well, if you plug that value into the numerator and denominator, how will $y = 4.7 \times 10^{-11}$ compare to 3.0×10^{-5}? The value of y is way too small to make a dent in 3.0×10^{-5}; thus, the values in the numerator and denominator would not change with y. If you iterate, you will get the same number and that means you're done. The second dissociation step ends as follows.

$[HCO_3^-] = 3.0 \times 10^{-5}$ M
$[H^+] = 3.0 \times 10^{-5}$ M
$[CO_3^{2-}] = 4.7 \times 10^{-11}$ M

The concentrations of H^+ and HCO_3^- remain 3.0×10^{-5} M as determined for the first step; they are unchanged in the second step to the allowed sigfigs. This will be true within our limit of coverage. A consequence of this coverage is that $y = K_{a2}$ as is seen in this last calculation. If you remember this, you won't even need to set up for a calculation for the second dissociation.

This ends the polyprotic example with all steps weak. Now let's go strong.

. . . .

Example 7. 0.100 mol H_2SO_4 is dissolved in 1.00 L solution. What are $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and pH at equilibrium?

. . . .

For H_2SO_4, the first step is strong but the second step is weak. For these cases, you <u>must</u> work with both steps. We begin with the first.

First dissociation $\quad H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$

This is strong, so everything goes to the right as is done for any strong acid. The initial 0.100 M H_2SO_4 goes completely to 0.100 M H^+ and 0.100 M HSO_4^-. This much is automatic for a strong step.

For the second step, we do the usual equilibrium calculation.

Second dissociation $\quad HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

$$K_{a2} = \frac{[H^+]\,[SO_4^{2-}]}{[HSO_4^-]} = 0.010$$

Set up a table. As done in the follow-up to Example 6, the initial amounts for the second step come from the final amounts for the first step.

	$[HSO_4^-]$	$[H^+]$	$[SO_4^{2-}]$
Initial:	0.100	0.100	-0-
Changes:	$-x$	$+x$	$+x$
Equilibrium:	$0.100 - x$	$0.100 + x$	x

Plug in.

$$K_{a2} = \frac{[H^+]\,[SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.100 + x)\,(x)}{0.100 - x} = 0.010$$

Approximate? With a K_{a2} of only 0.010, this is risky. But we'll do it anyway.

$$K_{a2} = \frac{(0.100 + x)\,(x)}{0.100 - x} \approx \frac{(0.100)\,(x)}{0.100} = 0.010$$

Solving for x gives 0.010. Iterate.

$$K_{a2} \approx \frac{(0.100 + 0.010)\,(x)}{0.100 - 0.010} = \frac{(0.110)\,(x)}{0.090} = 0.010$$

Now you get $x = 0.0082$, which is way different from 0.010. Iterate again.

$$K_{a2} \approx \frac{(0.100 + 0.0082)\,(x)}{0.100 - 0.0082} = \frac{(0.108)\,(x)}{0.092} = 0.010$$

$x = 0.0085$, not too far off. Iterate again.

$$K_{a2} \approx \frac{(0.100 + 0.0085)\,(x)}{0.100 - 0.0085} = \frac{(0.108)\,(x)}{0.092} = 0.010$$

$x = 0.0085$, same as prior. Stop.

Plug that into the table for $[H^+]$, $[HSO_4^-]$ and $[SO_4^{2-}]$.

$[HSO_4^-] = (0.100 - 0.0085)\text{ M} = 0.092\text{ M}$
$[H^+] = (0.100 + 0.0085)\text{ M} = 0.108\text{ M}$
$[SO_4^{2-}] = 0.0085\text{ M}$

From $[H^+]$, you will find pH = 0.97.

If you do quadratic method on this one, you will get $x = 0.0084$, which is acceptably close to 0.0085. This will give you the same answer anyway for $[H^+]$ and $[HSO_4^-]$ to the correct sigfigs. It does change the answer for $[SO_4^{2-}]$ a tad but, as pointed out earlier, we accept a difference of one in the final sigfig for the different methods.

These Examples 6 and 7 are fairly typical of a dissociation problem for a polyprotic acid. Polyprotic problems can look intimidating, but each type involves only one weak equilibrium calculation. Here it is in summary.

For a diprotic with both steps weak, you only do a full equilibrium calculation for the first dissociation. The second dissociation is ignored unless you need its product anion, in which case its concentration has the same value as K_{a2}.

For a diprotic whose first step is strong, you simply send the first step all the way to full dissociation, and you do a weak calculation starting from there.

Our Examples were limited to diprotics. You can do triprotics along a similar approach; all common triprotic acids have all weak steps, so you would follow the method of Example 6.

This concludes our acid dissociation calculations. Before moving on, let's consider a different kind of issue. The acids cited thus far have covered a range of K_a values, from strongs all the way down to $K_a = 1.0 \times 10^{-10}$ for phenol and even lower for hydrogen anions such as HPO_4^{2-}. We will now take a brief look at why there is such a range.

55.4 Strong, weak and weaker

The thermodynamic parameters of weak acid dissociation were mentioned for acetic acid in Section 54.1, for which $\Delta H° = -0.25$ kJ and $\Delta S° = -92.1$ J/K. In general, enthalpies for acid dissociation can run negative or positive. Acetic acid and others with K_a values in the range of 10^{-3} to 10^{-5} can go either way, exothermic or endothermic. Weaker acids ($K_a < 10^{-5}$) typically have endothermic dissociation, while acids not as weak ($K_a > 10^{-3}$) run exothermic. Thus and overall, $\Delta H°$ can favor or oppose dissociation. $\Delta S°$, however, will be negative and oppose dissociation for all weak acids, and this effect can be considerable. Why is $\Delta S°$ so negative? A neutral acid is dissociating to form two ions; the hydration of these two ions will involve ion-dipole along with the associated orientation effects. In addition, there is very strong hydrogen bonding for the H^+ cations and, to a lesser extent, for the basic anion; this will impose further orientation effects and all effects together decrease entropy considerably.

Let's look a bit more at the enthalpy contribution, $\Delta H°$, for dissociation in general.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

When comparing acid strengths of different acids, the $H^+(aq)$ part of this equation is the same for all. So what factors are involved in this process? First, the H–A bond is broken ionically, and there will always be some cost associated with that. Second, an O–H bond is formed ionically within protonated water ($H^+(aq)$) and that releases some energy. (This part is the same for all acids.) Third, there's a change in hydration energies: hydration of A^- will be greater than hydration for HA due to ion-dipole interactions, and that will release some energy. How these factors compare will determine the sign and the magnitude of the $\Delta H°$ for the overall dissociation.

As always, it is the specific combination of $\Delta H°$ and $\Delta S°$ which determines a specific $\Delta G°$, which then determines a specific K. For acid dissociations, the bottom line is that the values of $\Delta G°$ don't change much, but that still has a sizeable effect on K_a. This goes back to a point made in Section 51.2.

❝ The value of K is very sensitive to the value of $\Delta G°$ due to their exponential relationship.

$$K = e^{-\Delta G°/RT} ❞$$

Back then, a table was given for $\Delta G°$'s varying by hundreds of kJ's in ± directions, and the respective K's varied by huge numbers. Now in the case of acid dissociation, values of $\Delta G°$ will span only tens of kJ's, but even this will affect K_a substantially. Consider a new table covering some dissociation values for $\Delta G°$.

$\Delta G°$ (kJ)	34.2	28.5	22.8	17.1	11.4		−11.4	−17.1
K_a	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	. . .	10^{2}	10^{3}

Here, each column of $\Delta G°$ changes by a mere 5.7 kJ, which is small. Nevertheless, each 5.7 kJ translates into a factor of 10 for K_a, which is sizeable. Thus, small changes in chemical properties between different conjugate pairs can have a sizeable effect on K_a. Note the cases of negative $\Delta G°$ in the table; these apply to strong acids. Although we tend to equate all strongs as equally strong in water, they can still differ in $\Delta G°$.

So what kind of chemical properties have an impact on acidity? That depends.

There are many different categories of acids, and comparisons across the categories are not straightforward. Within a category, however, trends can sometimes be identified which indicate why some acids are better or weaker than others, but even these are subject to subtleties of $\Delta H°$ and $\Delta S°$. We will consider two trends.

The first trend involves polyprotic acids: each successive dissociation is harder to do. Thus, $K_{a2} < K_{a1}$ and $K_{a3} < K_{a2}$ for a particular acid. The reason for this is as follows. Consider H_3PO_4 again.

First dissociation step $\quad H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$

Second dissociation step $\quad H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

Third dissociation step $\quad HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

After each step, you end with a more negative ion. It's harder to pull H^+ off a more negative ion, so the next step costs more in enthalpy. Also for each step, the more negative ion is worse for entropy. Overall, each step is more and more opposed by $\Delta H°$ and $\Delta S°$, and each step is weaker.

The second trend is for oxyacids. Oxyacids contain a central atom Z bonded to one or more oxygens, one or more of which are bonded to hydrogen. A generic formula is $(HO)_xZO_y$ with $x \geq 1$ and $y \geq 0$. There are many such acids and many of these are very common; among these are H_2SO_4, H_3PO_4 and HNO_3, which are the top three acids produced industrially worldwide. Other examples include H_2CO_3, $HClO_4$, $HClO_3$, etc. In all of these here, the H's are bonded to O's, despite the way the formula is written. For oxyacids in general, there are two comparisons to note for acid strength. First, for one specific element Z, the K_a increases (better acid) when more O's are present. More O's present also means the oxidation number of Z is higher, so we can also say that K_a increases as the oxidation number of Z increases. As an illustration, there are four oxyacids for Cl and their strengths run $HClO_4 > HClO_3 > HClO_2 > HClO$. (The ON's for Cl in that series run 7, 5, 3, 1.) Second, for a specific formula but different element Z, then K_a increases as the electronegativity of Z increases. For example, the strengths for the HZO series for the halogens runs HClO > HBrO > HIO.

Enough of acids for now.

Problems

1. True or false.

    a. In a weak acid solution, dilution favors dissociation.

    b. Perchloric acid is diprotic.

    c. Water can deprotonate bisulfate ion (at least to some extent).

    d. The K_a of $H_2PO_4^-$ is greater than the K_a of HPO_4^{2-}.

    e. $HClO_3$ is a stronger acid than $HClO_2$.

2. Write the balanced equation for acid dissociation and write the K_a expression for each of the following.

    a. HBrO   b. HCN

3. Write the balanced equations for each step of dissociation for the following polyprotic acids.

    a. malonic acid, $HO_2CCH_2CO_2H$ (diprotic: the H's on the O's dissociate)

    b. H_3AsO_4 (triprotic)

4. Which of the following acids are monoprotic?

    nitric acid   phosphoric acid   oxalic acid   chlorous acid   carbonic acid

5. Pyrophosphoric acid, $H_4P_2O_7$, is tetraprotic, meaning it is capable of losing four H^+. Write the balanced equation and the K_a expression for the fourth step.

6. A 150. mL solution is prepared using 0.0198 mol butyric acid, $C_3H_7CO_2H$. What are the concentrations of $C_3H_7CO_2H$, H^+ and $C_3H_7CO_2^-$ at equilibrium? What are the pH and the percent dissociation?

7. 0.0268 mol of chloroacetic acid, $ClCH_2CO_2H$, is dissolved in water to make 800. mL of solution. What are the concentrations of $ClCH_2CO_2H$, H^+ and $ClCH_2CO_2^-$? What are the pH and the percent dissociation?

8. Vinegar is a mixture of various components, and the dominant acid component (and also the dominant smell) is acetic acid. The acid content can vary, typically around 5% w/w. As a comparative sample, consider a solution which contains 5.14 g CH_3CO_2H dissolved in water to give 100. mL solution. What is the pH of this solution?

9. A solution is prepared using 0.124 mol $H_2C_2O_4$ in a volume of 1.00 L. What are the concentrations of $H_2C_2O_4$, H^+ and $HC_2O_4^-$? What is the percent dissociation of $H_2C_2O_4$? What is the concentration of $C_2O_4^{2-}$?

10. Like sulfuric acid, selenic acid is also strong in the first step and weak in the second; $K_{a2} = 0.018$. A 200. mL solution of H_2SeO_4 is prepared using 0.00740 mol H_2SeO_4. What is the pH of the solution?

11. Of the following acids, which one is the strongest? Which one is the weakest?

    $HClO$ $HClO_2$ $HClO_3$ $HBrO_3$ $HBrO_2$ HIO

12. Calculate $[H^+]$ and the pH of carbonated water when the pressure of $CO_2(g)$ above the solution at 25 °C at equilibrium is 4.0 atm. (Here's a start. Set up the solubility equilibrium for $CO_2(g)$ and also set up the first dissociation step for $CO_2(aq)$. Add these two equations together. Find $\Delta G°$ for the sum equation from free energies of formation and use that to find K.)