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## A. Introduction

This handout follows Strong Acids. It leads to the final handout, on Buffers. In these last two handouts, there will be considerable emphasis on qualitative ideas rather than just calculations.

## B. Weak acids: overview

Acids give off hydrogen ions. A good question is: what is the $\left[\mathrm{H}^{+}\right]($or pH$)$ of an acid solution? Well, the first consideration must be: what is the acid concentration? 1 M HCl has more $\mathrm{H}^{+}$ions than 0.1 M HCl . But the next consideration is: how many $\mathrm{H}^{+}$ions do we get for each acid molecule? For strong acids, that is simple. By definition, strong acids ionize completely. Thus we can see how many $\mathrm{H}^{+}$we get per acid molecule just by looking at the chemical formula for the acid. (E.g., HCl gives one $\mathrm{H}^{+}$per HCl .) This was the subject of the preceding handout, on Strong Acids.

Weak acids are not strong, are not completely ionized. Thus we need to specify how much ionization occurs (the "degree of ionization"). That is, we need to supply one more piece of information for weak acids. This is the basis of the additional complexity of dealing with weak acids.

The amount of ionization of a weak acid is usually given by the equilibrium constant, $\mathrm{K}_{\mathrm{a}}$. Sections C \& D guide you through the story of how $\mathrm{K}_{\mathrm{a}}$ relates to the ionization of a weak acid. They are the core of the new material here.

Acid-base buffers, which are common, make use of the behavior of weak acids. Thus the discussion here about weak acids is a prelude to the discussion of buffers in the next handout.

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C. Weak acids: an example; finding K }\mp@subsup{K}{a}{
```

Consider a 0.10 M aqueous solution of acetic acid. The following balanced equation describes how acetic acid ionizes in water:

$$
\begin{equation*}
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \rightleftarrows \mathrm{H}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \tag{1}
\end{equation*}
$$

Acetic acid is a weak acid; it is only partially ionized. (The double arrow in Eq 1 shows that the reaction is reversible.) How much is ionized? To talk about the degree of ionization of a weak acid, we introduce the equilibrium constant for the ionization (or "dissociation") of the acid, the acid constant, symbolized $\mathrm{K}_{\mathrm{a}} \ldots$

$$
\begin{equation*}
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \tag{2}
\end{equation*}
$$

[In the Water handout we noted an alternative way to write the water ionization, showing transfer of $\mathrm{H}^{+}$to a water molecule. The same alternative applies here, with the same comment. See Eq 1a-W.]

Eq 2 relates $\mathrm{K}_{\mathrm{a}}$ to the concentrations of the various chemical species. But what good does that do? We don't know any of the concentrations. [We do know how much acetic acid we added $(0.10 \mathrm{M})$, but some has ionized, so we don't know how much is left.]

One of the concentrations is easy to determine: $\left[\mathrm{H}^{+}\right]$. We just get out the pH meter and measure the pH . It is 2.87 . That means $\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-3} \mathrm{M}$. (Eq 5-W)

Now we need to think about our acetic acid solution -- and Eq 1 -- a little. We can't easily measure the other concentrations, but we can figure them out. This is important chemical logic.

Eq 1 tells us the stoichiometry of the ionization; it says that 1 mol of acetic acid ionizes to form 1 mol of hydrogen ions and 1 mol of acetate ions. Therefore, $\left[\mathrm{H}^{+}\right]$must equal $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$. (There is nothing else in this solution. Any acetate ions came from the same place as the $\mathrm{H}^{+}$ions -- ionization of acetic acid.) That is, $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]^{=} 1.35 \times 10^{-3} \mathrm{M}$.

Now we have two of the concentrations needed in Eq 2. How about [ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right]$ ? Well, we put $0.10 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$ in the solution. Some of it ionized. How much ionized? $1.35 \times 10^{-3} \mathrm{M}$, as discussed above. So the amount left must be $0.10 \mathrm{M}-1.35 \times 10^{-3} \mathrm{M}$. That is 0.09865 M . (That ignores SF. Hm. To the hundredths place, which is all we have in 0.10 , it is 0.10 M , same as the original concentration. Only a very small amount of the acid ionized, and the remaining concentration is almost all of what we started with. This is common with weak acids, and it is often very helpful to recognize it.)

We now know all three concentrations shown in Eq 2. Therefore, we can calculate $\mathrm{K}_{\mathrm{a}}$. Doing this, we find that $\mathrm{K}_{\mathrm{a}}$ for acetic acid is $1.8 \times 10^{-5}$. (Units? $\mathrm{M}^{2} / \mathrm{M}=\mathrm{M}$. But we often omit the units in K expressions.)

If $\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}$, then $\mathrm{pK}_{\mathrm{a}}=4.74$. (Recall Sect F of Water.) You should be able to interconvert pK and K values; some tables show one and some show the other.

## Problems

(These problems involve some other acids, in addition to acetic acid. You don't need to know their formulas. They all work the same way as acetic acid, just with different numbers. More about this commonality in Sect E.)

1. You measure the pH of 0.010 M acetic acid; it is 3.37. Calculate $\left[\mathrm{H}^{+}\right],\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$, [ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right], \mathrm{K}_{\mathrm{a}}, \mathrm{pK}_{\mathrm{a}}$.
2. The pH of 0.10 M formic acid is 2.37 . Calculate $\mathrm{K}_{\mathrm{a}}$.
3. The pH of 0.10 M benzoic acid is 2.59 . Calculate $\mathrm{K}_{\mathrm{a}}$ and $\mathrm{pK}_{\mathrm{a}}$.
4. Which ionizes to a greater extent, formic acid or benzoic acid?

* 5. Compare problem \#1 to the example. In going from the problem to the example, we added an additional 0.09 M of acetic acid (from 0.010 M in the problem to 0.10 M in the example). By how much did $\left[\mathrm{H}^{+}\right]$increase when we added the additional 0.09 M acetic acid? * 6 . By how much would $\left[\mathrm{H}^{+}\right]$increase if we go from 0.010 M HCl to 0.10 M HCl ?


## D. Given $\mathrm{K}_{\mathrm{a}}$, calculate pH

In the previous problems we made a solution of known concentration, and measured the pH . Direct knowledge of $\left[\mathrm{H}^{+}\right]($from pH$)$ and chemical logic allowed us to calculate $\mathrm{K}_{\mathrm{a}}$. In fact, this is a practical method for measuring $\mathrm{K}_{\mathrm{a}}$.

Of course, for common acids, $\mathrm{K}_{\mathrm{a}}$ is already known; you can look it up in a text or handbook. The more practical problem is to calculate the pH that you would expect for a particular weak acid solution (i.e., for a particular concentration of a particular acid, with known $\mathrm{K}_{\mathrm{a}}$ ). Logically, this is the reverse of the previous kind of problem. We start with a specific example, based on the same data as before.

## Example

Given a 0.10 M solution of acetic acid, with known $\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}$. What is the expected pH ?
Eq $1 \& 2$ are still fully applicable. Eq 1 will supply chemical logic, and Eq 2 will allow us to calculate $\left[\mathrm{H}^{+}\right]$.

What do we know? We know the numeric value of $\mathrm{K}_{\mathrm{a}}$, and we know the original concentration of acetic acid, the amount added ( 0.10 M , in this example). Since some of the acid is ionized and some is not, then the sum of the two forms, $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]+\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$, must total the original amount ( 0.10 M ).

We want $\left[\mathrm{H}^{+}\right]$. Let's call it x . We are going to solve for x .

Chemical logic: if $\left[\mathrm{H}^{+}\right]=x$, then $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=x$. Why? Because Eq 1 says that we get these two ions in a $1: 1$ ratio; if we get $x$ of one of them, we must also get $x$ of the other.
$\left[\mathrm{H}^{+}\right]=\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$if there is no other source of the ions. That's true in this case (because we have a solution of just acetic acid). Sometimes it isn't true, and we must take that into account. We will see how to do this in the Buffers handout.

What is $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ ? Well, we started with 0.10 M acetic acid, and x of it ionized.
(Remember, Eq 1 says that 1 mol of acetic acid gives 1 mol of each ion. Or, to be a little more precise, it says that each mol of acetic acid that ionizes gives one mol of each ion.) Therefore, $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.10-\mathrm{x}$.

Now substitute what we know -- and have figured out -- into Eq 2:

$$
\begin{equation*}
1.8 \times 10^{-5}=\frac{x * x}{0.10-x}=\frac{x^{2}}{0.10-x} \tag{3}
\end{equation*}
$$

This is now a well-defined expression for x . We have one equation and one unknown. Just solve it for x , and we have $\left[\mathrm{H}^{+}\right]$.

Unfortunately, Eq 3 is slightly messy to solve. So we now need to discuss equation solving a little. This isn't very chemical -- except for one key assumption we will soon make.

There are two ways to deal with Eq 3.

One way is to solve it rigorously. The equation is quadratic. You can always solve a quadratic equation with the famous quadratic equation. It's tedious, but not really difficult if you use a calculator. (And maybe you have a computer program that solves quadratic equations almost as fast as addition.)

The second way is to use chemical logic to make a good approximation that simplifies the equation.

Look at the denominator of Eq 3; it says that $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.10-\mathrm{x}$. Yes. But this is a weak acid. Weak acids are only slightly ionized. Therefore -- and this is the assumption, based on chemistry -x is probably much less than $0.10 ; \mathrm{x} \ll 0.10$, in mathematical form. If $\mathrm{x} \ll 0.10$, then 0.10 -x is very nearly $0.10 ; 0.10-\mathrm{x} \sim 0.10$. That is, we can neglect the x in the denominator.

With this approximation, Eq 3 becomes $1.8 \times 10^{-5}=x^{2} / 0.10$. This is still a quadratic equation, but it is easier to solve (because it lacks the $\mathrm{x}^{1}$ term). Just multiply both sides by 0.10 , and take the square root (on your calculator). In this case, you get $\mathrm{x}=1.3 \times 10^{-3} \mathrm{M}$. This is $\left[\mathrm{H}^{+}\right]$, and it is also $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$.
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.10-1.3 \times 10^{-3}=0.0987-$ if you assume all digits are significant; this number is only about $1 \%$ from 0.10 M . Thus the approximation we made in solving the equation seems justified. (Note that the $\left[\mathrm{H}^{+}\right]$corresponds to pH 2.9 , in agreement with the original problem.)

Is the approximation $0.10-\mathrm{x} \sim 0.10$ always ok? No. It depends on the amount of ionization, on how weak the acid is. After you do a calculation with the approximation, you should check the answer to see if the approximation did turn out to be true. If not, you can do successive reiterations, or use the quadratic equation.

Our purpose here is to see the general behavior of weak acids. The approximation of low ionization will be adequate for (almost) all the problems that I give.

## Problems

7. Calculate the pH of 0.010 M acetic acid, given that $\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5}$.
8. The $\mathrm{K}_{\mathrm{a}}$ of formic acid is $1.8 \times 10^{-4}$. What is $\left[\mathrm{H}^{+}\right]$in a 0.10 M solution?
9. For benzoic acid, $\mathrm{pK}_{\mathrm{a}}=4.19$. Calculate the $\left[\mathrm{H}^{+}\right]$and pH for a 0.10 M solution.

Note that these problems involve the same data as the problems of Sect C. The general point is that Eq 2 involves four quantities. Typically, you know one of them ( $\left[\mathrm{H}^{+}\right]$or $\mathrm{K}_{\mathrm{a}}$ ) and the original acid concentration. Using chemical logic, based in part on Eq 1, you can figure out two more quantities in Eq 2. This leaves you with one unknown, which you then calculate.

## E. A variety of weak acids

The examples in the previous sections used acetic acid. The problems also introduced two other weak acids, formic acid and benzoic acid. We noted there that you didn't even need the formulas of the various acids, because they all work the same way, just with different numbers.

In fact, we can write general versions of Eqns $1 \& 2$. Consider an acid HA. What's A? It's the "other end" of the acid, whatever is left after $\mathrm{H}^{+}$comes off. The discussion of weak acids and the calculations do not depend on what A is. For the general acid HA, Eqns $1 \& 2$ become:

$$
\begin{equation*}
\mathrm{HA}(\mathrm{aq}) \rightleftarrows \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq}) \tag{4}
\end{equation*}
$$

$$
\begin{equation*}
K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]} \tag{5}
\end{equation*}
$$

This is why you were able to do the problems in the previous sections for new acids without knowing their formulas.

To do: Make a table showing the acids that we have discussed in this handout. Include hydrochloric acid in the table. Columns should include: acid name, formula, $\mathrm{K}_{\mathrm{a}}, \mathrm{pK}_{\mathrm{a}}$. Also, add two more columns for features of 0.10 M solutions: $\left[\mathrm{H}^{+}\right], \mathrm{pH}$. You can fill in most of the entries based on the Examples and Problems above. (You may need to leave a few entries
blank for now.) Put the acids in the table in some logical order. Spread the table out so that you can add some more acids to it later; you might even want to make the table on your computer. (The "completed" table is given in the answer section, for \#23.)

Weak acids vary in having different values of $\mathrm{K}_{\mathrm{a}}$. Eq 5 shows that $\mathrm{K}_{\mathrm{a}}$ varies with $\left[\mathrm{H}^{+}\right]$. Higher $\mathrm{K}_{\mathrm{a}}$ means more ionization, higher $\left[\mathrm{H}^{+}\right](=$lower pH$)$. Your table should show that the order of the acids by $\mathrm{K}_{\mathrm{a}}$ and by $\left[\mathrm{H}^{+}\right]$(of 0.1 M solution) is the same. Lower $\mathrm{K}_{\mathrm{a}}$ means less $\mathrm{H}^{+}$, lower ionization -- means that the acid is weaker.

We have now subdivided and compared weak acids. Weak acids are acids that ionize incompletely. If we compare two weak acids, the weaker one (lower $\mathrm{K}_{\mathrm{a}}=$ higher $\mathrm{pK}_{\mathrm{a}}$ ) ionizes less (at a given concentration).

You will find lists of weak acids, with their $\mathrm{K}_{\mathrm{a}}\left(\right.$ or $\left.\mathrm{pK}_{\mathrm{a}}\right)$, in textbooks and handbooks. Sometimes there is a list of acids in order of weakness, without $K_{a}$ being noted. Some tables also include some strong acids; see following section.

## F. So where do strong acids fit in this picture?

We started our discussion of acids by distinguishing strong and weak acids. We now see that weak acids can be ranked by how weak they are, by their value of $K_{a}$. Are strong acids fundamentally a distinct class, or just a matter of degree? The latter. Strong acids are acids with very high $\mathrm{K}_{\mathrm{a}}$. Strong acids are acids which ionize to a great enough extent that, for practical purposes, we consider them fully ionized.

When we use Eq 5 to calculate $\left[\mathrm{H}^{+}\right]$, the denominator term will be of the form $[\text {acid }]_{\text {final }}=$ [acid] $]_{\text {original }}$ - [ions], as in Eq 3. For weak acids, [ions] $\ll$ [acid $]_{\text {original }}$; we often approximate the denominator as [acid $]_{\text {original. }}$. For strong acids, $[$ ions $] \sim[a c i d]_{\text {original; }}$; the denominator approaches zero, making $\mathrm{K}_{\mathrm{a}}$ quite large.

Recall the discussion of whether the denominator approximation of neglecting the x term is always valid. Obviously it isn't for strong acids. But there also are intermediate cases: some fairly strong weak acids, with $\mathrm{K}_{\mathrm{a}}$ values that are "fairly high". These acids aren't strong enough to be considered fully ionized, and not weak enough that the denominator x term can be neglected. The math gets messier, but there is no real complication of chemistry. Acids have a wide range of $K_{a}$ values. For very high $K_{a}$, we can make the approximation that ionization is complete. For very low $\mathrm{K}_{\mathrm{a}}$, we can make the approximation that ionization is negligible.

## G. More problems and questions

Questions. These are intended as qualitative. You should have a reason for each answer.
10. Which will give the higher $\left[\mathrm{H}^{+}\right], 0.05 \mathrm{M}$ lactic acid or 0.20 M lactic acid? $\left(\mathrm{K}_{\mathrm{a}}=1.4 \times 10^{-4}\right.$. $)$
11. Continuing... Which will give the higher pH ?
12. Which is more acidic, 0.10 M acetic acid or 0.10 M hydrochloric acid?
13. Which would give the higher $\left[\mathrm{H}^{+}\right], 0.01 \mathrm{M}$ boric acid $\left(\mathrm{K}_{\mathrm{a}}=7.3 \times 10^{-10}\right)$ or 0.01 M carbonic
$\operatorname{acid}\left(\mathrm{K}_{\mathrm{a}}=4.45 \times 10^{-7}\right)$ ?
14. Continuing... Which is the stronger acid, boric acid or carbonic acid?
15. Continuing... Which of those two acids would give the higher $\left[\mathrm{H}^{+}\right]$, if each solution was 0.14 M ?
16. Which would give the higher $\left[\mathrm{H}^{+}\right], 0.05 \mathrm{M}$ hydrofluoric acid $\left(\mathrm{HF} ; \mathrm{pK}_{\mathrm{a}}=3.45\right)$ or 0.05 M formic acid $\left(\mathrm{pK}_{\mathrm{a}}=3.75\right)$ ?
17. Which would give the higher $\left[\mathrm{H}^{+}\right], 0.05 \mathrm{M}$ phenol (carbolic acid; $\mathrm{pK}_{\mathrm{a}}=10.00$ ) or 0.05 M nitrous acid $\left(\mathrm{HNO}_{2}, \mathrm{~K}_{\mathrm{a}}=4.5 \times 10^{-4}-\right.$ don't confuse it with nitric acid)?

* 18. Trichloroacetic acid, often called TCA, is a derivative of acetic acid. Its $\mathrm{pK}_{\mathrm{a}}$ is 0.70 . Do the Cl atoms of TCA make the compound more or less acidic than acetic acid?
* 19. An acid is listed with a $\mathrm{pK}_{\mathrm{a}}$ that is negative. Does the negative $\mathrm{pK} \mathrm{K}_{\mathrm{a}}$ indicate that the acid is quite strong or quite weak? (Hint: Take a specific numeric example, and calculate $\mathrm{K}_{\mathrm{a}}$.)
* 20. Which is more acidic, 0.05 M acetic acid or 0.50 M formic acid? $\left(\mathrm{K}_{\mathrm{a}}\right.$ values are in earlier problems.)
* 21. Which is more acidic, 0.50 M acetic acid or 0.05 M formic acid?
* 22. Which is more acidic, 1.0 M acetic acid or 0.50 M HCl ?


## Problem

23. For each acid introduced in the above questions, calculate the pH of a 0.10 M solution. Add these acids to the table you started in Sect E. You should be able to fill out all the columns, except for some formulas. (Special case: $\mathrm{K}_{\mathrm{a}}$ for TCA is high enough that the denominator approximation is not appropriate. If you know how to solve Eq 5 for TCA, fine; otherwise leave these entries blank. You can still add TCA and its $\mathrm{K}_{\mathrm{a}}$ to the table.)

## H. Polyprotic acids [briefly noted]

Some acids give off more than one $\mathrm{H}^{+}$(per acid molecule). However, each one comes off separately, with its own $\mathrm{pK}_{\mathrm{a}}$.

Example. Phosphoric acid, $\mathrm{H}_{3} \mathrm{PO}_{4}$, ionizes to $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$(the dihydrogen phosphate ion). The acid constant for this is called $\mathrm{K}_{\mathrm{a} 1}$, the first ionization constant for phosphoric acid. $\mathrm{K}_{\mathrm{a} 1}=$ $7.1 \times 10^{-3}$.
$\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$then ionizes to $\mathrm{HPO}_{4}{ }^{2-}$ (the hydrogen phosphate ion). The acid constant for this is $\mathrm{K}_{\mathrm{a} 2}$ for phosphoric acid; it can also be thought of as $\mathrm{K}_{\mathrm{a}}$ for the dihydrogen phosphate ion. $\mathrm{K}_{\mathrm{a} 2}=$ $6.2 \times 10^{-8}$. And of course, there is a third step in this case. The three parts of Eq 6 show the three steps:

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \rightarrow \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} & \mathrm{K}_{\mathrm{a} 1}=7.1 \times 10^{-3}  \tag{6}\\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \rightarrow \mathrm{H}^{+}+\mathrm{HPO}_{4}{ }^{2-} & \mathrm{K}_{\mathrm{a} 2}=6.2 \times 10^{-8} \\
\mathrm{HPO}_{4}{ }^{2-} \rightarrow \mathrm{H}^{+}+\mathrm{PO}_{4}^{3-} & \mathrm{K}_{\mathrm{a} 3}=4.4 \times 10^{-13}
\end{array}
$$

So the basic idea of working with polyprotic acids is the same as for the acids we have already discussed. Each step involves one $\mathrm{H}^{+}$, as in Eq 4 . However, the calculations become more complex, because more than one acid is present. The secret to working with acid mixtures,
including those from polyprotic acids, usually is making good chemical assumptions about which is the major equilibrium.
(One polyprotic acid sneaked into the earlier problems (\#13): carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$. The $\mathrm{K}_{\mathrm{a}}$ given in the problem, $4.45 \times 10^{-7}$, is actually $\mathrm{K}_{\mathrm{a} 1} . \mathrm{K}_{\mathrm{a} 2}=4.7 \times 10^{-11} . \mathrm{K}_{\mathrm{a} 1}$ is quite low, $\mathrm{K}_{\mathrm{a} 2}$ is much lower, and the second ionization is negligible in a simple solution of carbonic acid.)

## I. Sulfuric acid [briefly noted]

In Strong Acids (Section C) we noted that sulfuric acid, $\mathrm{H}_{2} \mathrm{SO}_{4}$, is a common strong acid. However, it is more complicated than the other strong acids because it is diprotic and the second $\mathrm{H}^{+}$comes off as weak. We are now able to deal with this.

Consider $0.10 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$. We know that one $\mathrm{H}^{+}$comes off as strong. This gives us $0.10 \mathrm{M} \mathrm{H}^{+}$. We know that the second $\mathrm{H}^{+}$comes off as weak. Even before we look up the $\mathrm{K}_{\mathrm{a}}$ for this second ionization, we know that we will get somewhere between 0 and $0.1 \mathrm{M} \mathrm{H}^{+}$from the second ionization. Adding together the two ionizations, we see that $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ will give somewhere between 0.1 and $0.2 \mathrm{M} \mathrm{H}^{+}-$depending on how strong the second ionization is. This is already useful information.

The second acid constant for sulfuric acid, $\mathrm{K}_{\mathrm{a} 2}$, is $1.0 \times 10^{-2}$. (Note that this is the $\mathrm{K}_{\mathrm{a}}$ for the hydrogen sulfate ion, $\mathrm{HSO}_{4}{ }^{-}$.) That's rather high for a weak acid, and in dilute solutions the second ionization is substantial. You can do calculations using Eq 5, as for other weak acids, above. However, for this high a $\mathrm{K}_{\mathrm{a}}$, the denominator approximation that ionization is negligible is usually not appropriate. Therefore, you need to solve the equation rigorously.

## J. Weak bases [briefly noted]

The idea of weak bases is just like the idea of weak acids. For weak bases, the increase in $\left[\mathrm{OH}^{-}\right]$is less than expected from the amount of chemical added, due to incomplete ionization.

## Example

A common weak base is ammonia, $\mathrm{NH}_{3}$. Ammonia doesn't donate $\mathrm{OH}^{-}$, but it can take (or "accept") $\mathrm{H}^{+}$(to make the ammonium ion, $\mathrm{NH}_{4}{ }^{+}$). And since $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$are inversely proportional (recall Eq 3-W), taking $\mathrm{H}^{+}$is equivalent to giving off $\mathrm{OH}^{-}$.

The base reaction for ammonia is...
(7) $\quad \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

The expression for the base constant, $\mathrm{K}_{\mathrm{b}}$, is...

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

The important point for now is to see that these equations are logically similar to the earlier equations for weak acids. The logic of doing calculations for weak bases is the same as presented earlier for weak acids.

Another weak base of interest is the acetate ion, $\mathrm{CH}_{3} \mathrm{COO}^{-}$. That may surprise you at first. But recall Eq 1 . Acetic acid molecules give off $\mathrm{H}^{+}$, leading to acetate ions. The reaction is shown in Eq 1 as reversible. Acetate ions can accept $\mathrm{H}^{+}$, giving acetic acid molecules. As we saw with $\mathrm{NH}_{3}$, accepting $\mathrm{H}^{+}$is the behavior of a base; thus acetate ion is a base. (We say that acetate ion is the conjugate base of acetic acid.) This is conceptually important when we discuss buffers, in the next handout.

## K. Answers

## $\underline{\text { Sect C }}$

1. $\left[\mathrm{H}^{+}\right]=4.27 \times 10^{-4} \mathrm{M} .\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=\left[\mathrm{H}^{+}\right] .\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=0.0096 \mathrm{M} \sim 0.010 \mathrm{M} . \mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-}$
${ }^{5}$. (That is the same as in the example; $\mathrm{K}_{\mathrm{a}}$ itself does not depend on concentration.) $\mathrm{pK}_{\mathrm{a}}=4.74$.
2. $1.8 \times 10^{-4} \quad 3.6 .6 \times 10^{-5} ; 4.18$
3. Formic acid (Lower pH , higher $\left[\mathrm{H}^{+}\right]$, higher $\mathrm{K}_{\mathrm{a}}$.)
4. $9.2 \times 10^{-4} \mathrm{M}$ (About $1 \%$ of the added acetic acid ionized.)
5. 0.09 M (It's all ionized; a strong acid.)

Sect D
$\begin{array}{lll}\text { 7. } 3.37 & 8.4 .24 \times 10^{-3} \mathrm{M} & 9.2 .54 \times 10^{-3} \mathrm{M} ; 2.60\end{array}$
$\underline{\text { Sect G (If the reasons aren't clear, please ask.) }}$
10. 0.20 M lactic acid (Same acid, so higher concentration will give more $\mathrm{H}^{+}$ions.)
11. 0.05 M lactic acid ( pH and $\left[\mathrm{H}^{+}\right]$are inversely related. High pH means less acidic.)
12. 0.10 M HCl ("More acidic" means higher $\left[\mathrm{H}^{+}\right]$, or lower pH . The concentrations of the two acids are the same. Which is stronger? You should recognize these common acids: HCl is strong, acetic acid is weak.)
13. 0.01 M carbonic acid (Higher $\mathrm{K}_{\mathrm{a}}$.)
14. carbonic acid (We are now using "stronger" and "weaker" as comparative terms. Higher
$\mathrm{K}_{\mathrm{a}}=$ more ionization = "stronger".)
15. carbonic acid (If both are at the same concentration -- any concentration, but same for both -- the carbonic acid solution will have higher $\left[\mathrm{H}^{+}\right]$.)
16. 0.05 M HF (Lower $\mathrm{pK}_{\mathrm{a}}=$ higher $\mathrm{K}_{\mathrm{a}}$.)
17. 0.05 M nitrous acid (You are given one acid constant as $\mathrm{K}_{\mathrm{a}}$, one as $\mathrm{pK} \mathrm{K}_{\mathrm{a}}$. Convert one to the other form before comparing them.)
18. more acidic (Lower $\mathrm{pK}_{\mathrm{a}}$.)
19. strong (Negative $\mathrm{pK}_{\mathrm{a}}$ is very low. Low $\mathrm{pK}_{\mathrm{a}}$ means high $\mathrm{K}_{\mathrm{a}}=$ strong acid.)
20. 0.50 M formic acid (Both the acid and the concentration are different, so be careful. But in this case there is more of the stronger acid. That is, formic acid "wins" on both concentration and strength.)
21. ??? (There is more acetic acid, but formic acid is stronger. I wouldn't try to predict which solution is more acidic without doing the calculations.)
22. 0.50 M HCl (Again, concentration and strength point in opposite directions. But there is only a little more acetic acid, and we know HCl is much stronger. It seems a safe bet that the 2-fold greater amount of acetic acid won't make up for its weakness.)
23. This table is in order of decreasing $\mathrm{K}_{\mathrm{a}}$ or $\left[\mathrm{H}^{+}\right]$.

|  |  |  | 0.1 M solution |  |  |
| :--- | :--- | :---: | :---: | :---: | :---: |
| acid name | formula | $\mathrm{K}_{\mathrm{a}}$ | $\mathrm{pK}_{\mathrm{a}}$ | $\left[\mathrm{H}^{+}\right], \mathrm{M}$ | pH |
|  |  |  |  |  |  |
| hydrochloric acid | HCl | high | low | 0.1 | 1.00 |
| TCA | $\mathrm{CCl}_{3} \mathrm{COOH}$ | $2.0 \times 10^{-1}$ | 0.70 | $7.30 \times 10^{-2} *$ | 1.14 |
| nitrous acid | $\mathrm{HNO}_{2}$ | $4.47 \times 10^{-4}$ | 3.35 | $6.69 \times 10^{-3}$ | 2.17 |
| hydrofluoric acid | HF | $3.53 \times 10^{-4}$ | 3.45 | $5.94 \times 10^{-3}$ | 2.23 |
| formic acid | HCOOH | $1.78 \times 10^{-4}$ | 3.75 | $4.22 \times 10^{-3}$ | 2.37 |
| lactic acid | $\mathrm{CH}_{3} \mathrm{CHOHCOOH}$ | $1.41 \times 10^{-4}$ | 3.85 | $3.75 \times 10^{-3}$ | 2.43 |
| benzoic acid | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$ | $6.46 \times 10^{-5}$ | 4.19 | $2.54 \times 10^{-3}$ | 2.59 |
| acetic acid | $\mathrm{CH}_{3} \mathrm{COOH}$ | $1.76 \times 10^{-5}$ | 4.75 | $1.33 \times 10^{-3}$ | 2.88 |
| carbonic acid | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $4.45 \times 10^{-7}$ | 6.35 | $2.11 \times 10^{-4}$ | 3.68 |
| boric acid | $\mathrm{H}_{3} \mathrm{BO}_{3}$ | $7.3 \times 10^{-10}$ | 9.14 | $8.54 \times 10^{-6}$ | 5.07 |
| phenol | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}$ | $1.0 \times 10^{-10}$ | 10.00 | $3.16 \times 10^{-6}$ | 5.50 |
|  |  |  |  |  |  |

Formulas for the organic acids are shown as condensed structural formulas.
There are other ways to write them.

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11/5/02

