Lab 11B • 05/29/12

What's an acid? A compound that loses a proton. Is that the only definition of an acid that we have? pH < 7? No. A compound that accepts lone pairs. We're going to limit our discussion to hydrogen, because pKa is related to hydrogen's dissociation. Why is it that hydrogen is defined as an acid, H+? What's the context? What's it based [ha!] on? Water. The idea is that water, all by its little self, can dissociate into hydrogen and hydroxide ions; this is [the] Arrhenius definition of acids and bases: that an acid is something that specifically generates H+, and a base is something that specifically generates OH- – that's because the two of them combine to make water. Is this a favorable process? No. Why would hydrogen and hydroxide want to pull apart from each other, because you're breaking a bond and separating charge in order to do that.

Why does it happen if it's unfavorable? Why does water evaporate at room temperature? What's vapor pressure? Some of the molecules have enough energy in order to be able to evaporate. In this case, some of the molecules have enough energy in order to be able to dissociate. Since that number depends on temperature, then the automatic amount of H+ that exists in solution at any one time also depends on temperature. That means that pH = 7 only means neutral at one temperature. [riffing on ph 7] The auto-ionization of water is unfavorable, but happens to a small degree, since at any temperature, a few molecules will have enough energy in order to be able to dissociate. [energy distribution graph]

Kw is the equilibrium constant that, since water is a pure substance, we leave it out of the equilibrium expression; we just get the product of the two ions. It happens to be at [some particular temperature] that it's equal to 1.0×10^{-14}. [temp for 1g/ml; 1 cal; triple point] In pure water, the concentration of H+ is equal to the concentration of hydroxide, because if all you have is water to start with, it's just going to make those two different ions. You plug x in for either of them, you get $x^2 = 1.0 \times 10^{-14}$, which means these are equal to 1.0×10^{-7} M. Then, we have pH, which is defined as the $-\log_{10}[H+]$; in this case, it will be equal to exactly 7. pH 7 means neutral only at this temperature.

Organic example of acid dissociation – acetic acid dissociating to make acetate and H+. Since these are all in the same phase, they're all part of the solution, they all do go into the equilibrium constant. To simplify, we'll see that there's a hydrogen there; in this case, A stands for both acetate and acid, where generally use HA to simplify writing out an equilibrium expression. HA makes the conjugate A- and an H+. [The] acid dissociation constant is products over reactants; it looks like this. Turns out that you talk about bases the same way. The Arrhenius acid/base definition has to do with generating H+ and generating OH-. In organic chemistry, we don't use that definition; we use the Brønsted-Lowry definition, which focuses instead giving up an H+ and accept and H+. Accepting an H+ ends up being the same thing in terms of Arrhenius acids and bases, because it's the hydroxide that would be accepting that H+. If I want to show a base dissociation, I would take a compound like ammonia, when it reacts with water, it causes hydroxide to be produced, plus ammonium ion. If we were to write this as B, neutral in this case, now we're making the acid conjugate, and we could write a Kb expression for this, which would be products over reactants. In this case, it's hydroxide that ends up on the top.

What happens if A- and B are the same thing? What if we're talking about the same compound that's going in reverse directions. If we took Ka and multiplied it by Kb, we'd get [math expression]. But remember, A and B are the same thing; I can cancel the A and B, I can cancel the HA and HB. I'm left with H+ and OH-, which is equal to Kw. This leads us to the mathematical demonstration that an acid's strength, which is measured by Ka, must be inversely proportional in water to its conjugate base's strength. In other words, the more that an acid wants to give up a proton, the less that whatever forms afterwards wants to get that proton back. [equilibrium explanation] As this equation shows, an acid's strength is inversely proportional to it's conjugate base's strength.

In water, what is the strongest base you could possibly have? OH-. So if we say we have something like a ketone. What's the pKa of a ketone? 19. Can you measure the pKa of a ketone in water? No. Because if you had a deprotonated ketone, wouldn't it just instantly react with water to make hydroxide, and really you'd just be measuring hydroxide? Let's take a more extreme example – let's say that we had an alkyne, pKa 25. That just turns into hydroxide in water, so how do you measure it? Some of these pKa values, you have to estimate or you have to use other solvents in order to determine the values of them.

If we're leading up to titration, we need to be able to talk about what the H+ concentration is in solution for some particular kind of compound. Since we're starting out with acetic acid, let me ask you these questions: if I had 1M hydrochloric acid versus 0.1M hydrochloric acid versus 0.01M hydrochloric acid, what would be the pH of each of these solutions? 0, 1, and 2. Why could we jump to that automatically? What is the definition of a strong acid? Heavy spontaneous dissociation, which means large Ka, which means small pKa. The pKa of hydrochloric acid is much less that zero. If it's much less than zero, that means Ka is much greater than 1, much greater than 1000. That means that nearly every molecule of hydrochloric acid dissociates when it's in water. That's why we can look at a 1M solution of HCl and say: oh, that means we have 1M H+. If we have 1M H+, $-\log_{10}[1] = 0$. 0.1 is 10^{-1}; $\log 10^{-1} = -1$, negative of that is 1. 2.

But guess what? They're not quite true. Why? Why do you think this effect, this deviation from prediction is more extreme for the more concentrated solution? Why wouldn't every molecule dissociate?

Activity – it's the idea that, in solution, it you have so many ions around, even if it might be favorable for them to dissociate, they might be crammed together where, in a sense, they're forced to be kinda associated with each other, even though they're technically not. You can form what's called an ion pair; they dissociate, technically, but they act together. In terms of colligative properties, that would reduced the number of particules you think are around. [ionization factor in colligative properties] If you had sodium chloride, you'd say: multiply everything by two, cause sodium does its thing, chlorine does its thing. But the real value is something less that 2, because you don't always get those ions totally separated from each other. That's this concept of activity; that's why these pH values deviate slightly from what you'd predict. The ions interfere with each other; higher concentration – more ions, more interference, more deviation from ideal behavior. When solutions are highly concentrated, interactions between solute ions [particles] cause deviation from predicted solution behavior. [activity leads to equilibrium constants]

ICE problem

You have a 1M solution of acetic acid; what's the pH? Given 1.0M acetic acid, and ignoring activity, what is the pH? The pKa of acetic acid is 4.76, so that means the Ka is 1.76×10^{-5}. Turns out that's exactly the kB of ammonia. How do I use this information to calculate the pH of acetic acid? What we do for ICE problems is to set up what our reagents are, what our product are, and try to predict what our concentrations will be at the beginning of the process, how it's going to change during that process, and then what the end of that process is. ICE stands for initial/change/[end]equilibrium. What would the be initiation HA concentration? 1.0M, because I told you you have a 1M solution. What would be the initial H+ concentration? 10^{-7} – in water, if you're dealing with water, it has an automatic concentration, and at room temperature, roughly, it's 10^{-7}. But 10^{-7} compared with 1, it's such a small, small correction, that in this case, we're going to ignore it. It is an issue if you have a super dilute solution of a weak acid – the auto-ionization of water becomes a competitive process. A-, no matter what, is going to be zero; at the instant we dump it in the water, we're pretending it hasn't had time to dissociate yet. If it's a weak acid, it's going to dissociate, which means what? That the acid disappears by some value x. Since thre is a 1:1:1 stoichiometry between these, H+ is going to up by x, as well as A-, so we end up with 1-x, x, and x.

We could do this the easy way or the hard way? What's x going to be, roughly? Small. 1 - small = 1. Under certain conditions, it could be ignored. [acid vs ka factor of 100? rules use to justify simplification] Let's say that we can do it in this case, just to get some kind of rough value. We would say Ka is products over reactants, so $x \cdot x / 1-x = 1.76 \times 10^{-5}$. If we ignore that x, then we get $x^2 = 1.76 \times 10^{-5}$. $x = 4.19 \times 10^{-3}$. If we substitute that back in right now, you could see now, it is compared to 1. If I did this the quadratic method, if I didn't simplify, I'm going to get an answer that's close enough to begin with that, yes, it was justifiable to make that simplification. If I take the -log of that, then I get 2.38.

What would happen if I were to add solid sodium hydroxide, enough to neutralize exactly half of this solution, how would we calculate that pH? Let's reframe the question: you have prepared a buffer solution of exactly a half more of acetic and and a half mole of sodium acetate. What would be the pH of that buffer solution? To use these Ka's, if you have a neutralization, you take care of the neutralization first and then we can go back and do a calculation. In other words, Ka doesn't have hydroxide in it as a reagent. [don't try to create overall neutralization expression] [Instead], every bit of hydroxide that is there, we get rid of some of the acetic acid and make acetate, to reframe the question in terms of just the compound that's doing the dissociating, not the neutralization itself. Imagine if I give you both an acid and its conjugate; how do we then calculate the pH in solution? Given the two things, what is the pH?

The answer's 4.76; this is the same situation at the half-equivalence point. Half-equivalence means half of the acid we had has been neutralized. This is the situation that you have: if I started out with 1M acetic acid, if I neutralized half of it, half it's still acetic acid, half of it's been converted, so it's exactly this situation. At the half-equivalence point, pH = pKa. The pKa is 4.76, so the answer is 4.76 – approximately. It's that approximate part that I'm wanting to show you. We'd still do an ICE problem. We have 0.5M acid; we're going to have 0.5M conjugate. We're going to say 0 for H+, even though we know it's not. What's going to happen? Is x going to be a negative or a positive number? [how can this be determined?][if H+ 0, some has to form][0.5 - x, x, 0.5 + x]. Ka = $1.76 \times 10^5 = (0.5 + x)(x)/(.5-x)$. If we make that same simplification that x itself is really really tiny, we can't eliminate x entirely; you can't a factor. But you could for both the [0.5 + x] and [0.5 - x] simplify. We get $0.5 \cdot x / 0.5$, which just gives us x. If $x = 1.76 \times 10^{-5}$, the pH = 4.76, which is equal to the pKa. But if that value of x is not small, then we can't make this simplification. This is exactly the same kind of simplification that comes from the Henderson-Hasslebach equation. If I had this idea situation, where I put in exact equal amounts of acid and base, another way of stating this is there's going to be some shift; a little bit of acid will turn into base, a little base will turn into acid, but if the solution is dilute enough, and if the acid is weak enough, that little shift won't matter.

Let's look at the definition of this equilibrium expression. Let's say that we arbitrary established that there were certain concentrations of HA and A-. [justification of simplification] What if they don't [shift?] Let's rewrite this. Let's take the -log10 of both sides of the expression.What do we get? -log10 of Ka is pKa. When you take the log of a product, it's equal to the sum of the logs, so I'm going to split the next part up. We'll get -log10 H+ + -log10 A- / Ha. I'm going to rewrite that. This will become pKa = pH - log10(A-/HA). Flipping this part of the expression around, we therefore get pH = pKa + log10 [A-]/[HA], which is the Henderson-Hasslebach equation.

This only works if the same assumption above works: that we can ignore the small shift in equilibrium that occurs once you make a solution of an acid and its conjugate. [common situation – make buffer of particular kind – prepare x volume of solution that's going to have this particular pH value; you have to know how to work the with pH to get back to [the] concentrations to get back to amounts of the two things that were together in solution.

Titrations

Let's say that we had an unknown solution of acetic acid – unknown in the sense that we don't know its concentration, but we know it's acetic acid. We're using sodium hydroxide as the base to titrate. Why is sodium hydroxide one of the best choices of a base to titrate with? Sodium hydroxide completely dissociates, [so] we don't need to worry about accounting for the base strength if we're trying to figure out something out the acid. The fact that we're using sodium hydroxide lets us not worry about the sodium hydroxide and focus entirely on what's going on with the acid [because of water definition].

Let's say that we have unknown concentration. Let's say, for argument's sake, we know that we have a 0.1000M solution of sodium hydroxide. In a standard, classic titration, we have two burets: one that has the acid, one that has the base.You would have a reaction flask that, if we were doing this qualitatively – meaning not from instrumentation not observation – what would we put, then, into that flask, that reaction flask? In other words, I've got classic set-up of an acid buret and a base buret, and then I had a reaction flask, we add water to. Does it matter what kind of quantity of water we add to this solution? No, not as long as its neutral water, cause it's not going to increase or decrease the H+ concentration – at least for the purposes of stoichiometry. Of couse, adding water's going to change the pH, but we're not looking at that, necessarily, when we're doing a titration. If all we want to know is how many moles are reacting with how many moles, no, it doesn't matter how much water we put in there. If we're not using a pH meter, what else do we need? We need an indicator. Is phenolphthalene always the right indicator to use for an acid/base titration? No, because an indicator's color change approximately 1 pH unit to either side of its pKa value. In other words, the optimum place for an indicator is also the optimum place for a buffer solution [of the indicator], which is at the half-equivalence point, which is when the pH = pKa. When you take an indicator, you want to have one where its pKa is the same pH as the solution's pH once neutralization is complete. The indicator for a titration is chosen such that the pKa of the indicator is the same as the expected pH of the neutralized solution. [phenolphthalein has a pKa right around but just higher than 7, which is basic], which is exactly what you'd expect from the neutralization of acetic acid and sodium hydroxide. Because, neutral is not the same thing as neutralized.

What does the term neutral mean? If you say it means pH 7, [it's incorrect]. At only one temperature does this situation cause water the have a pH of 7, because the amount of H+ and OH- in solution depends on temperature, but this is always correct: that regardless of temperature, when you have pure water, when it auto-ionizes, these two concentrations are going to be the same. What does neutralized mean? Moles of acid = moles of base. Why would moles acid not be the same thing as moles H+? Acid is not the same thing as H+; base is not the same thing as OH-. Why? Because if you have a weak acid or base, you don't get one H+ from each acid; you get a fraction of that. If you have different acid and base strengths, then the amount of H+ and OH- that are produced are different, which is why neutral is not the same thing as neutralized. If a weak acid and/or a weak base are used in titration, the moles of H+ or OH- – whichever's appropriate – would not be the same as the moles of acid or base – whichever is appropriate – since incomplete dissociation would occur.

Neutralization os acetic acid with sodium hydroxide, would we end up with an acidic solution or a basic solution? [Is acetic] a strong acid or a weak acid? Weak. Sodium hydroxide – strong base or weak base? Strong. They're going to make a basic solution. Base strong, acid weak; base wins. Once acetic acid and sodium hydroxide neutralize each other, you produce sodium acetate. Is sodium acetate, as a salt, acidic or basic? Basic, because sodium acetate is the conjugate base of acetic acid. Acetic acid is a weak acid that does not want to dissociate; if you make sodium acetate, which means you force the complete dissociation of acetic acid, then the moment we add acetate back to solution, it wants to establish again an equilibrium with the acetic acid, which means that the sodium acetate reacts with water, which means you produce hydroxide, which means you end up with a basic solution. Once acetic acid is fully neutralized by sodium hydroxide, a salt is produced; that's sodium acetate. This product is effectively the result of forced complete dissociation of a weak acid. Once completed, that salt will want to re-establish equilibrium with the acid, so it will react with water, which forms hydroxide, resulting in a basic solution.

The goal of this is to get when moles of acid equals moles of base, because that is the equivalence point in a titration. What is the endpoint of a titration? Why are these two things different? A visual change, your eyes are only so good, so they might not catch right when the exact correct is to stop. Another way to [state] that is: even if you had supreme observational skills, what if one drop was too much to add in to solution – that you're almost done neutralizing, that you're less that a drop away. You could measure the volume right before the drop and right after, but neither are quite correct – that's the endpoint: where you see the change, which is going to be slightly different from where the change really happens. The equivalence point is where our goal is. The endpoint and the equivalence are close enough that we ignore the difference. But if you chose the wrong indicator, for example, your endpoint's going to be way off from your equivalent point; this is why you have to choose the right indicator to make sure these two events happen at the same time. The endpoint is the visual observation that a titration is complete; that means a color change.

Let's construct a titration curve. What does the curve look like? This presumes that we are using a pH probe; we might still use an indicator anyways to let us know that we really are close to the endpoint. pH is our x-axis; generally, it is the volume of titrant that is the x-axis. In other words, as we add specific quantities of sodium hydroxide to this acidic solution, how does the pH change? We have two burets: one acid, one base. We have the indicator that we add to a solution of the acetic acid we want to titrate. If we start out with just the acid, that means we're going to start out way closer to the pH 0 side of things. What will this titration curve look like? If I had a 1.0M molar solution of HCl, then, ignoring activity, what would the solution of that pH be? 0. If I had 0.1M HCl, that's pH 1; if I had 0.01M HCl, that's pH 2; 0.001M, pH 3. To get from pH 0 to pH 1, you have to neutralize 90%; to get from pH 0 to ph 2, you have to neutralize 99%. You have to go most of the way to being complete to change 1 pH unit, in this example. To get the next pH unit, it only takes one tenth of that – that's a 90% change versus a 9% [overall] change. To get to the next pH unit overall, is 99.9%, but that is just 1/100th of the original journey. If you're adding base linearly, before adding at the sample place, 90% of the time you're only going to change 1 pH unit, in this example. You're still adding at the same place. The next pH unit only takes one tenth that time. The last few units all happen so quickly that you're pH curve shoots up like this; that's why pH curves have this kind of shapes to them. As titrant is added at a linear pace, pH, at some point, changes exponentially.

It is at the steepest point of that curve that we have the equivalence point. The reason for showing that titration curve, if we're talking about acid/base strength, is what happens at the half-equivalence point. If we have neutralized half of our acid, At half-equivalence, the amount of acid is roughly equal to the amount of base – I say roughly, cause remember: we have a -x factor [in the numerator] that we ignore; if we ignore it, then this expression becomes equal, not a constant. [equilibrium] If it's true, then we say that Ka is = [H+][A-]/[HA], but because we're saying HA and A- are equal to each other, that leads us to Ka = H+, which leads us to pKa = pH. If you do a titration, you get to the equivalence point; with an indicator, you would just go until the point of color change, with a pH probe, you would go past that point, look at the graph, find the steepest point on that graph, and find the volume for the equivalence point. You would then take half that volume and find out whatever the pH is there; that pH will equal the pKa. How do I get moles? Don't need them.

Now the stoichiometry aspect. At equivalence point, we say that the moles of acid are equal to the moles of base. We're generally not dealing with solids if we're dealing with solutions, so we substitute. We could say that the molarity of the acid times the volume of the acid is equal to the molarity of the base times the volume of the base, because moles is molarity times volume because molarity is moles solute per liter solution; we're measuring out the solution, so the units cancel appropriately to leave us moles. The molarity of the acid is the unknown, the volumes we measure, and the molarity of the base is either calculated or standardized. KHP [is] a reasonable analog to acetic acid [to use as a standard]; KHP, a solid that can measured out in much more precise proportions. You could then use a volumetric flask to prepare a solution that would have four significant figures in its concentration; we use that as the reference solution, then, because if you know that concentration of a base, and then you know the volume of acid and base used, you know three of the four variables in a four-variable equation, which means you can solve for the concentration of the acid.

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The auto-ionization of water is unfavorable but happens to a small degree since @ any temperature a few molecules will have enough energy to dissociate.

$K_w = [H+][OH-] = 1.0 \times 10^{-14}$ at only one temperature. In pure water @ ???°C, $[H+]=[OH-]=1.0 \times 10^{-7}M$
$pH \equiv -\log_{10}[H+] = 7.00$
pH = 7 means neutral only @ this temperature
$Ka = [H+][A-]/[HA]$

An acid's strength is inversely proportional to its conjugate base's strength
Strong acid: Heaving spontaneous dissociation –> large Ka –> small pka
pKa (HCl) << 0

When solutions are highly concentrated, interactions between solute particles can cause deviation from predicted solution behavior –> activity

Weak acids

Given 1M acetic acid (and ignoring activity) what is the pH? pKa = 4.65; Ka = 1.76x10^-5

Give 0.500 M acetic acid & 0.500 M sodium acetate, what is the pH?

If x is not small compared to 0.5, this simplification is not possible.
When an acid & a conjugate are added together, a small shift in their concentration will occur. But, if the acid is weak, that shift can often be ignored.

Titration

Indicator – The indicator for a titration is chosen such that the pKa of the indicator is the same as the expected pH of the neutralized sol'n.
Neutral ≠ neutralized
If a weak acid and/or weak base are used in titration, the moles of [H+]/[OH-] would not be the same as the moles of acid/base, since incomplete dissociation would occur.
Once acetic acid is fully neutralized by sodium hydroxide, a salt is produces (sodium acetate). This product is the result of the forced complete dissociation of a weak acid. Once formed, the salt will thus want to re-establish equilibrium with the acid, so it will react with water, forming hydroxide, resulting in a basic solution.
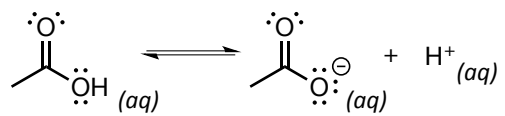
Equivalence point – When equal moles of acid & base have been reacted
Endpoint – The visual observation that a titration is complete (color change).

As titrant is added linearly, pH changes exponentially.

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998

Structures

05/29/12 lab • 1

05/29/12 lab • 2

unknown
concentration