

## Lab 11A • 05/30/12

What is an acid? Anything that dissociates to make a proton? Or, we have this alternate definition of something being an electron acceptor. We have the Arrhenius definition; we have the Brønsted-Lowry definition; we have the Lewis definition of acids and bases. The Lewis definition has to do with electron pairs. When we come up with pKa values, we're generally discussing things that do dissociate to make H<sup>+</sup>; the broadest definition that covers that conceptualization is the Brønsted-Lowry definition, where an acid something that generates H<sup>+</sup>. Under that definition, what would a base be, then? Something that accepts H<sup>+</sup>. That's a broader definition that [the one usually taught to grade school students]. What's an even more fundamental definition? That a base something that explicitly dissociates to make hydroxide. Ammonia is a very common base that would fail to be classifiable under that definition, because ammonia does not dissociate to make hydroxide; it will react with water, cause water to make hydroxide, but in the formula NH<sub>3</sub>, there is no OH. That is, however, where we get our definitions of acids and bases originally. Why? Because the fact that, in water, there's always some proportion of H<sup>+</sup> and OH<sup>-</sup> ions in solution. This is called the auto-ionization of water.

Would this auto-ionization be something favorable? Would auto-ionization be something that's a favorable process? No, because you're breaking a bond and you're trying to separate out ions. Why does it happen if it's unfavorable? Equilibrium; if an equilibrium can happen, it will happen. What's another way of expressing it not using equilibrium? [Le Châtelier's is still related to equilibrium][energy distribution graph] If you have some distribution of molecular energies, if you have a barrier that the molecules have to cross for some kind of reaction or process to occur, at any temperature there'll at least be a few molecules that have that energy to dissociate. The auto-ionization of water is an unfavorable process that does occur to some degree at any temperature, since there will always be a fraction of molecules that have the energy to dissociate. There is an equilibrium constant for this process, [which is] called Kw. In this process, since water is declared a liquid, it's a pure substance, it's not given a concentration, even though technically we could take 1000g of water, which at a certain temperature is 1L, and calculate that that's equivalent to 55.5M. If we leave it out of this expression, we only get the H<sup>+</sup> and OH<sup>-</sup> concentrations. That product has a value of 1.0x10<sup>-14</sup> at only one temperature [quote it].

In pure water, at this temperature [triple point T, density of 1 T, specific heat of 1 T, pKw of 14 T], the hydroxide ion concentration's going to be equal to how much H<sup>+</sup> that you have; if you were to substitute into Kw, it leads us to the fact that the hydrogen ion concentration would be 1.0x10<sup>-7</sup> M. How? If the [hydrogen's] concentration's the same as hydroxide – that's true because you get one molecule breaking up into one of each of these – then if we call H<sup>+</sup> x, then OH<sup>-</sup> is also x, we get x<sup>2</sup> = 1.0x10<sup>-14</sup>, which how we get x, which is H<sup>+</sup>, being equal to 1.0x10<sup>-7</sup>. There's then this way of measure called pH, which is defined as the -log<sub>10</sub> of that H<sup>+</sup> concentration, so it would be equal to 7.00. But, pH = 7 means neutral at only one temperature. Why is this true? The H<sup>+</sup> and OH<sup>-</sup> concentrations change; that's because not necessarily due to intermolecular forces changing, but the fact that more molecules could dissociate, because that there's dissociation in the first place is due to molecular energy distribution. As we increase temperature, we increase the number of molecules that are able to undergo this dissociation, which means you have more H<sup>+</sup> than OH<sup>-</sup>. Even though you might still have a neutral solution, neutral doesn't have anything to do with pH 7, because pH is just a measure of H<sup>+</sup> concentration. It just happens to work out coincidentally at this right temperature, we get this nice, easy-to-remember number, which is why [we are programmed to say]: neutral means pH 7. That's garbage. [have to program pH meters with temperature to take into account varying dissociation due to energy available]

An acid is something that makes H<sup>+</sup>; a base, presumably, is something that makes OH<sup>-</sup>, but now we're going to work with that more expanded definition where we focus on the H<sup>+</sup> instead, because many organic molecules accept an H<sup>+</sup> but don't have a hydroxide. Within that kind of definition, when we're still dealing with H<sup>+</sup>, or at the very least, if we say we're still dealing with aqueous solutions, then there's a couple of things we could write down. For example, we could quantify the likelihood that some particular acid is going to dissociate – not due to being neutralized, but just by itself to dissociate. Using the typical organic example of acetic acid, notice that in this case, acetic acid and with what it turns into, these are all water solution, so if we have water as the solvent, all three of things are going to end up in the equilibrium constant, because they are in the same phase. If acetic acid is an acid, then how can we refer to what's produced here, the acetate? What is its relationship to acetic acid? It is its conjugate. Very frequently for these kinds of processes, we abbreviate. Generally, the A in HA means acid, but this happens, coincidentally, to be acetate as well. Using that simplified representation, we could say that the equilibrium constant for that dissociation is  $[H^+][OH^-]/[HA]$ .

We could also, though, talk about a Brønsted-Lowry base and what would happen to it in water. This could be classified as a hydrolysis reaction. We again have a mixture of phases, here. Water, being a pure substance, we would ignore in whatever equilibrium constant we could write. Let's make the same type of simplification of structure: B for base. B reacts with water to produce two things: hydroxide and it's [B] acid conjugate. We have a base and its conjugate. We could write a Kb that is products over reactants, so  $[HB]$ , the conjugate, times hydroxide, over B itself. Let's just say, for the sake of argument, that A and B are the same thing – meaning, for example, I started about acetic acid dissociating, then I switched to talking about ammonia. What if, instead, I was talking about acetate? The product of acetic acid itself reacts with water. If we let acetate dissociate completely, it doesn't want to be in that situation, cause it is something that is in equilibrium.

If you throw acetate by itself in water, sodium acetate, you're going to cause a reverse reaction. We could put acetate as our base example. If we make A and B the same compound, we're talking about different conjugates, what happens if we multiply  $K_a$  and  $K_b$ ? That would give us  $[H^+][A^-]/[HA] * [OH^-][HB]/[B]$ . If I say A and B are the same thing, then A and B cancel, HA and HB cancel, which means we end up with  $[H^+][OH^-]$ , which is  $K_w$ . This definition falls out this way because we are assuming the base reaction occurs in water.

On a purely mathematical basis – not understanding physically what's going on – just look at this expression we could say an acid's strength, which is measure by this  $K_a$ , more dissociation, bigger  $K_a$ . Dissociation is the strength of an acid, how much does it break about, and acid strength is inversely proportional to its conjugate base's strength.

What is the strongest base that can survive in water? Let's say if you took bromobutane, made a Grignard reagent, react it with water, what do you get? Grignards act like really strong bases, so the Grignard would just pull a hydrogen off water, making an alkane. But what's left over? Hydroxide. What happens if we reacted sodium borohydride with water? What do we get? Hydroxide. What happens if we take a [terminal] triple bond, deprotonated it, and throw it into water; what are we going to make? Hydroxide, because water is a stronger acid than all of these other compounds you're making bases out of? Once you add the water, they react, they neutralize; all you're left with hydroxide.

How can you measure the  $pK_a$  of something like a triple bond? That carbon-hydrogen bond's got a  $pK_a$  of 25, when nothing can exist in water [as its conjugate] with a  $pK_a$  of water's own  $pK_a$ . How do we measure  $pK_a$  then? There's only some limited  $H^+$  concentration; there's only some limited  $OH^-$  concentration. If you have an acid stronger than  $H^+$ , it would react to turn into  $H^+$ ; if you had a base stronger than hydroxide, it would just turn into hydroxide. That answer is: you can't; you have to use other solvents or other techniques in order to get those  $pK_a$  values. There are limits of what can exist in aqueous solution, because there's limits on what water itself can handle.

If I have a strong acid, then what's the definition of that? You have extensive or complete dissociation – extensive, spontaneous dissociation. If you dissociate a bunch, that means you have more products than reactants, so your  $K_a$  is going to be large, which means you'll have a small  $pK_a$ .  $pK_a$  has a similar definition as pH; it's the  $-\log_{10}$  of the  $K_a$  constant. We often use  $pK_a$  instead of  $K_a$ , because it's easier to memorize small numbers with a few digits instead of things like  $1.82 \times 10^{-23}$ . HCl is a strong acid. If I had 1.0M or 0.1M or 0.01M HCl, what would the pH of a 1.0M HCl solution be. What would be the pH of a 1.0M solution of hydrochloric acid? What's the definition of pH? The concentration of  $[H^+]$  in solution. Is HCl a strong acid? Yes, it's got a negative  $pK_a$ , which means it has 99.% dissociation. The assumption we generally make is if you have 1 mol of acid, then it makes 1 mol of  $H^+$ ; if we have 1 M acid, we presume that we have 1M  $H^+$ . If we have 1M  $H^+$ , the pH is 0. 1 is  $10^0$ ; log means take the exponent off of the 10.  $\log_{10}(10^0)$  is zero. Tenth molar HCl,  $10^{-1}$ ; log of  $10^{-1}$  is -1; the  $-\log_{10}$  of  $10^{-1}$  is therefore 1. For centimolar, which is  $10^{-2}$ , that means it's going to be a pH of 2.

Except it's not. Why do these pH value not come out to be what we expect them to be? [activity coefficients] If we expect something to fully dissociate, that means that ions pull apart from each other and have nothing else to do with each other. But what happens when we start getting really concentrated solutions? It may be that there are so many ions in solution that they're not exactly put together to make a compound, but in solution, we have a solvent that we don't talk about very much. Particularly when water's a solvent, water forms these things called solvent cages. in other words, you'll have, like an onion, a layer of water molecules at the center, and then another layer of water molecules around that, and another layer of water molecules around that. Ions, to transport through solution, they have to be able to break through those cages, which are not like iron bars, it's just water molecules, so things can slip through, but things can get surrounded at the same time. What if, somehow, a plus and a minus ion both get trapped in the same solvation sphere? Then they're dissociated, but they act like they're one particle in a way. [colligative properties,  $\Delta T = k \cdot m \cdot i$ ] The ionization constant tells you how much something wants to dissociate. For something like HCl, you'd expect that number to be 2, because you put in one HCl, you expect to get one  $H^+$  and one  $Cl^-$  out. But, if you have a concentrated enough solution, that doesn't happen. That means the effective concentration of HCl in solution is lower than the calculated concentration in solution. These activity values are associated with something known as chemical potential, which is a measure of energy. Since equilibrium is also a measure of energy, we use these chemical potentials to make an equilibrium constant. However, if you make certain simplifications, which we do, we end up using concentrations, not activity coefficients, in equilibrium constants. The real concentration that exists in solution is not necessarily the way that you prepared it because of this activity effect, and one of the manifestations of [differences in] activity is the formation of ion pairs – which in this case would mean that the  $H^+$  that you think you have available, you don't, which means the pH is a little higher than what you would calculate. When solutions are highly concentrated, interactions between solute particles can cause a solution to have behavior that deviates from ideal. That's quantified by this thing known as activity.

Let's talk about weak acids, which are acids that spontaneously only dissociate a very small amount. Acetic acid is [one of the] most common example[s] of a weak acid. Given a 1.0M solution of acetic acid, and ignoring activity, predict the pH of the solution. How do we solve this problem? What information will we need to solve this problem? ICE is the way to solve it, and you need the  $K_a$  value. The  $K_a$  of acetic acid is  $1.76 \times 10^{-5}$ , which means the  $pK_a$  is 4.76. Quite coincidentally, 4.76 is the  $pK_b$  of ammonia. What is this ICE problem?

It's short of initial/change/equilibrium[end], which means we look at a process, we identify what compounds we need to worry about in terms of their concentrations, we try to figure out what the concentrations are at the start of whatever process we're trying to calculate; we then determine how will those concentrations. We put together to get an expression for what we really think is going to exist in solution. Since this is a process that's governed by an equilibrium constant, we throw it back in the equilibrium constant and solve. To abbreviate, there's HA, the acids itself; H<sup>+</sup>, the acid that's generated, and A<sup>-</sup> that's generated as well.

Based on the information given in this problem, what would be the initial concentration of HA? 1, because you're given a 1 M solution. Of course it's going to dissociate, but that's the reason we set up the problem the way we are. We first think: what's in the solution the moment the solution is formed, before any kind of equilibrium is established. At that point, what's going to be the H<sup>+</sup> concentration? 10<sup>-7</sup>, because there's auto-ionization of water. Yes, we always call this zero for this kind of problem, [as long as we do not have] dilute solutions of weak acids. But if you had such things, then the auto-ionization of water becomes competitive, and we have to worry about. Since we have a concentrated solution of acetic acid, we'll ignore it and call it zero. Regardless of what that concentration is, what would A<sup>-</sup>, initially, before the solution has a chance to anything, what would it be? Zero. Of course, as soon as we through acetic acid in water, some of it dissociates. If it dissociates, that means it goes down in quantity, so we can represent that by -x. This is a 1:1:1 stoichiometric correspondance between HA and the H<sup>+</sup> and the A<sup>-</sup> produced, they'll each go up by that same quantity x, which means we get final concentrations of 1-x, x, x. We have the K<sub>a</sub>, which is [H<sup>+</sup>][A<sup>-</sup>]/[HA], which means we get  $1.76 \times 10^{-5} = x \cdot x / 1 - x$ , which means we're going to have to solve a quadratic.

Or will we? Why not? If we look at what our likely solution is going to be, x is going to end up being very tiny compared to the number 1. Whenever we multiply by x, we're not allowed to drop that out. If  $x = .000000001$ , then if we took 1- that value, we get .999999999, which is equal to 1, really, within the limits of whatever instrumentation used. If  $x \ll 1$ , it is allowable to ignore it to simplify the numbers. It's a very big if, though, cause it doesn't always happen. [when can simplification be made numerically?] Let's just solve this making the simplification and demonstrate to ourselves, on a numerical basis, that in this case it's acceptable. If I do get rid of that -x, then I get  $x^2 = 1.76 \times 10^{-5}$ , which means x is  $4.19 \times 10^{-3}$ ; that's equal to the H<sup>+</sup> concentration, so that leads us to the pH being 2.38. We see that x time 10<sup>-3</sup>, less that 1% of the value of the number 1. If we didn't simplify, we would have been off than maybe 1%, which for most purposes, that acceptable deviation; that's why we're able to make the simplification.

We need to find out when the Henderson-Hasselbach equation doesn't work.

Think about this: given 1 M acetic acid; let's say that we had 1 L of that 1 M solution. If somehow we were able to introduce 1/2 mole of sodium hydroxide in solid form, somehow without changing the volume, what would be the pH of the solution? If I have 1L of a 1M acetic acid solution, if I were to put in 1/2 mole of sodium hydroxide [while] somehow maintaining that 1L of volume, what would be the pH of the solution? The answer's 4.76, because I just described the half-equivalence point. If you get rid of half of the moles of your acid because you've added that amount of base, then you're left with half of the original acid, half of it is as its conjugate. When you have the acid and its conjugate in equal proportion, that's the half-equivalence point, which is the point where the pK<sub>a</sub> is equal to pH.

If we're given a neutralization [problem], the mistake that many people make is to write down acid plus hydroxide makes salt and water. If you're given a K<sub>a</sub>, that is for the dissociation of the acid; it has nothing to do with a neutralization equation. [You technically can take a K<sub>a</sub> and turn it into some kind of equilibrium constant and solve simultaneously for the acid, the hydroxide, whatever else gets formed, but it's a more complicated approach]. Why is hydroxide such an excellent base for these kinds of problems, not in terms of its chemical reactivity – why does it work out really well in terms of simplifying the problem that you have? It will make water. Once you make water, it disappears from many of the equations that you're dealing with – if we're dealing with equilibrium constants, if we're working in aqueous solutions and we make water, water no longer ends up in that equilibrium constant. Here's what we do: we take the original acid, we say: when hydroxide reacts with it, it's going to make water, so simply subtract the number of moles of base from the number of moles of acid, you've got the acid that's left. Once you do that, you're making some conjugate, so the number of moles of base add to the conjugate, because it's going to be produced from the acid. It then turns back into a standard problem, which you can then solve.

Let's say that we had a solution of 0.5 [M] acetic acid and 0.5 M sodium acetate. How would we calculate the pH of this solution? We do it as an ICE problem. Will the concentrations of acetic acid and sodium acetate be 0.5 M after equilibrium? If I prepared, by taking pure acetic acid and pure sodium acetate, put them both into a liter of solution, half a mole of each, will the solution actually exist this way? No, it won't, because there's a specific equilibrium between its acid and base form. If you put some arbitrary concentrations of the two together, they're going to shift a little bit, one way or another, in order to make equilibrium. If it shifts a lot, then we're not able to make any simplifications in our calculations. If it shifts hardly at, then as we're going to see, we can make some simplifications in our calculations. It's exactly this situation that determines: do we use the Henderson-Hasselbach equation or not? Let's see why and how.

First, let's solve the problem doing ICE, doing the formal method. We have HA representing the acetic acid; it's going to dissociate to make H<sup>+</sup>; we'll have A<sup>-</sup> as the conjugate.

What'll be the initial concentration of the acid? 0.5 [M]; when we set these problems up, even though we know it's wrong, we start with what we're given and see how will the equilibrium shift to get us to the right answer. What'll the initial concentration of base be? Also 0.5 [M]. What'll the initial concentration of [H+] be, effectively? Zero – it's not zero, but it's close enough that we can ignore it. If this is zero, then the only thing possible is for its value to go up. If we say it's zero and we say that equilibrium will occur when it can, equilibrium wants to make at least a little H+, so if we say we have zero H+, some H+ gets generated no matter what. If we have established that, that means we're going to use, if x is our increase, -x to show much of the acid dissociated to make that H+, which will at the same time make A-. So we end up with 0.5 - x, x, and 0.5 + x as our end values. To solve, we would put them in the equilibrium expression. Now we're in the same kind of situation, where we would have to otherwise solve a quadratic. If x was really small compared to 0.5, we could simplify. If  $x \ll 0.5$ ,  $0.5 - x = 0.5$  itself. We could do that for both the numerator and the denominator; why not, because if x is small and being ignored for one, it's automatically small enough to be ignored for the other one. That means that we get  $K_a = 1.76 \times 10^{-5} = x(.5)/(.5)$ , which means it's x, which is our H+ concentration. What that means is the pKa is roughly equal to the pH at that point. This expression is only true if the concentrations of an acid and its conjugate shift only slightly once the buffer solution is prepared, because this is a nearly ideal buffer solution – it's equal proportions of an acid and its conjugate [are ideal buffers 0.1 M?] This simplification only is valid if the concentrations of an acid and its conjugate do not shift substantially once the solution is prepared.

Where do we go next? Let's generalize this approach. By making that simplification, what we did is we stuck in the concentration for the acid in it's appropriate place, we stuck the concentration of the base in the appropriate place, no making the adjustment for equilibrium. Let's generalize that process. We do that by taking the Ka expression and rewrit[ing] it. Let's take the  $-\log_{10}$  of both sides of this expression.  $-\log_{10} K_a$  is pKa; the log of a product is the sum of the individual logs, so we can expand the righthand side to be  $-\log_{10} [H^+] + -\log_{10} [A^-/HA]$ .  $-\log_{10} [H^+]$  is pH, so you get  $pK_a = pH - \log_{10} [A^-/HA]$ . Rewriting that, we get  $pH = pK_a + \log_{10} [A^-/HA]$ , which that is then the Henderson-Hasselbach equation. You could also say that  $pH = pK_a - \log_{10} [HA/A^-]$ , because if you invert a fraction, it's the negative of its log. This equation only works if you can make exactly the type of simplification that we made just up above. We did a very special case of an ideal buffer solution, where an acid has the same concentration as its conjugate. If you look at what the result was, we cancelled out the -x and +x; that would have been the adjustments to these initial concentrations. If we say that the original concentrations won't shift much, then we generalize this way to solve the problem and we put it into the Henderson-Hasselbach equation. Why? Because if simply know the concentration of the conjugates, you can get the pH if those concentrations don't shift. In real life, you would get a problem like this: given a maximum of 100g of sodium carbonate and sodium bicarbonate, if you had 10L of solution that had biological pH, 7.2, how would you do it? What you would do is: you would look up the pKa of hydrogen carbonate, you would look at the pH you want, 7.2, you'd solve for the ratio of the concentrations. You would get that ratio of concentrations, convert those into moles, convert those into grams, figure how much of each of the reagents you would use, then discuss how you would prepare the solution. If we're talking about molarity, you add everything and fill up to the volume mark, not add that volume of liquid.

#### Titration – acetic acid with sodium hydroxide

$M_1V_1 = M_2V_2$ . If we're doing a titration, I'll write it as a forward-only reaction. Since this is, in fact, a standard Arrhenius acid/base titration, this follows the normal pattern of acid plus base makes salt plus water. The point of doing a titration is you want to get to the point where this is not a limiting reaction; in other words, you want to have exactly the same number of moles of acid with the number of moles of base, which is known as the equivalence point. At the equivalence point, the moles of acid is equal to the number of moles of base. But, we're not dealing with solids, we're dealing with solutions; if we take molarity and multiply by volume, that gives us moles. Molarity is moles solute / liters solution; we're measuring these whole bits of solution when we're titrating, so the units cancel and gives us moles. We'll substitute then: molarity of the acid times the volume of the acid is equal to molarity of the base times the volume of the base. Out of these four variables, we're able to measure or calculate three of them; the molarity of the acid, if this was a titration of a weak acid, is the unknown quantity. You have the volume of acetic acid, volume of sodium hydroxide that use that you would measure. Then, the molarity of the base, in certain titrations, maybe it would just be calculated, but [often the base] is instead standardized, which means before using the base, we would turn around and titrate the base with yet another acid, but one which itself would be the true reference compound, known as the primary standard. KHP [is often used as] a primary standard because although it is a dicarboxylic acid, one of them's already been deprotonated, so you only have one proton left, which makes it chemically very similar to acetic acid, which is the compound that we want to try to determine the concentration of. Since KHP can be measured out very accurately and precisely – it's a solid, so it's easy to measure, and if we were to handle it correctly, we could make sure that it does not absorb water – we could then use a volumetric flask, which would have four significant figures in its volume measurement, to make a solution that would have four significant figures in it[s concentration] for this reference KHP solution, which then reacts with the sodium hydroxide, so you can get sodium hydroxide's concentration, which you then use here to get acetic acid's concentration.

Physically, a titration set-up is often something like this: you have your acid buret, you have your base buret, you add a certain quantity of the unknown acid and water into a reaction flask. Does it matter how much water we add, in principle? No, because we're not trying to determine the pH of the solution during a titration; we could measure pH, but the idea is that you're looking for the equivalence point – equivalence point being when moles of acid equals moles of base, which has nothing to do with water. Whatever water you add to the solution at this point shouldn't matter.

What other thing do we need to add into solution? The indicator. What would indicator would be chosen for this kind of process? Phenolphthalein. Why is phenolphthalein chosen for the titration of acetic acid and sodium hydroxide? It changes color around the same pH we expect once the titration is completed. When this is done, will the solution be neutral? Of course it will not be neutral. If it's not neutral, then we need to make sure that whatever indicator we use changes its color at that same pH point, or else we're going to stop the titration at the wrong time. [chem 1b – pKa of indicator] An indicator tends to change its color at its own half-equivalence point. In other words, if you have an indicator that has a base form and an acid form and you put the exactly equal proportion of the two in solution, then end if you end up with more base or acid, that means it's going to flip colors on way or another. Within about 1 pH of the pKa of an indicator is the range over which an indicator's useful; you therefore want to make sure that you match your pKa of the indicator to the anticipated pH of the solution at the endpoint. An indicator is chosen so that the pKa of that indicator matches the anticipated pH of the titration mixture at the equivalence point.

What is the equivalence point? It's when the moles of acid equal moles of base. But there's this other thing called the endpoint; what is the endpoint? It's the place where the indicator changes color. If you didn't choose your indicator properly, then it may change colors, but not at the time where you actually have equal moles. Even if you did choose it properly, are the human eyes the best possible judge of a change in color? Even if they were somehow, what if you were just, just barely shy of being at the endpoint, and you were about to add a drop, but it turns out that you only need half a drop of solution to get to the endpoint. Are you going to be able to anticipate that and know to divide the drop in half somehow? No. The endpoint is the visual clue that a titration is completed; if properly done, it will be nearly identical to the endpoint, but not necessarily so. They're two distinct concepts. The endpoint is the visual indication that a titration is complete, meaning a color change [acid/base, redox, complexometric] If you wanted to do it more accurately, we would use a pH meter in these acid/base cases, because there's a particular point that we can find on that graph that we can ascribe to being the equivalence point.

Once we titrate acetic acid with sodium hydroxide, will we end up with a neutral solution. The answer to that is no. What does neutral mean? How do we know when something is neutral? It has nothing to do with acids and bases. A singularly fundamental definition.  $[H^+] = [OH^-]$ . In neutral water, you'll have equal proportion of  $H^+$  and  $OH^-$  generated; therefore, the definition of neutral is  $[H^+] = [OH^-]$ . pH = 7 doesn't mean neutral; pH 7 means  $[H^+] = 1.0 \times 10^{-7}$ . What's neutralized? The acid and base have the same number of moles. By acid, you cannot mean  $H^+$ , and by base, you cannot mean  $OH^-$ ; why? Why is one of these definitions focused on  $H^+$  and  $OH^-$ , and another one is focused on the acids and bases themselves? Why are these two different concepts? Let's say we limited our discussion to Arrhenius bases. Ka of acetic acid, if we round it, is  $1.0 \times 10^{-5}$ . Let's make it an even simpler number, let's round too far up, let's call it  $1.0 \times 10^{-4}$ . What would be the percentage of acetic acid that should dissociate in solution, roughly? The square root of  $10^{-4}$  is  $10^{-2}$ , which is 0.01, which is 1%. If 1% of acetic acid dissociates all by itself, that means given 1 mole of acetic acids, you have 0.01 mol of  $H^+$  [in 1 L of solution].  $H^+$  is not the same as moles of acid, so neutral is not the same thing as neutralized. Another way to say it is this: if I have an acid and a base react with each other, this acid makes some  $H^+$ , this base makes some  $OH^-$ ; if they don't produce the same amount, cause they're not the same acid/base strength, then you get an imbalance in how much  $H^+$  and  $OH^-$  are produced. For example, when you take acetic acid, which is a weak acid, and you force it to dissociate, then imagine if we just took sodium acetate, the conjugate, by itself and threw it into water. It wants to re-establish equilibrium with acetic acid, but there is not acetic acid, so it makes it by reacting with water. Acetate reacts with water, you make hydroxide, which means you make a basic solution, even though all you have is sodium acetate. Since sodium acetate is the product of neutralization of a weak acid and a strong base, that means a weak plus a strong base makes a strongly basic solution – strong beats out the weak. If a weak acid, or base, is used in titration, the number of moles of  $H^+$  – or if we're talking about base,  $OH^-$  – that are effectively generated by spontaneous dissociation will be less than the number of moles of the acid or base itself. The effect that this has is that neutral – which is when  $[H^+]$  and  $[OH^-]$  are equal – may not happen just because you do a neutralization; it means it's not the same thing as saying neutralized.

[If] you take acetic acid, which is a weak acid, and react it with sodium hydroxide, which is a strong base, you end up making a salt that is basic. Why? Because once acetic acid has been totally neutralized by the sodium hydroxide, a salt is produced that tries to re-establish equilibrium with its parent acid. Once we force this titration to the end, we force it out of equilibrium, so it tries to establish equilibrium. To do this, the acetate reacts with water, which produces hydroxide, which produces a basic solution. Weak acid, strong base; strong base wins, the solution is basic.

pH method. Start off with an acid, which means we're going to be closer to pH 0. We look at how the pH changes as we add sodium hydroxide. Because in this example it is the compound being used to quantify something about acetic acid, we refer to sodium hydroxide as the titrant. A curve will look something like this. The shape of this curve does depend on – do you have a strong acid and a strong acid, or do you have a strong acid/weak base, or do we have, like this case, a weak acid/strong base, a weak acid and [weak] base, are either of them polyprotic? The curve can have different forms. We're going to take this one case of weak acid/strong base. Since we're talking about acetic acid and sodium hydroxide, the steepest part of the curve here, which is the equivalence point, is going to happen above pH 7 – weak acid, strong base. Let's try to understand a little bit about the shape of this curve.

Let's pretend that we were titrating hydrochloric acid instead of sodium hydroxide. 0.1, 0.01, 0.001, 0.0001 M hydrochloric acid is going to produce, approximately, pH 1, pH 2, pH 3, and pH 4. As we go from one of these concentrations to the next, we're just going by one pH unit at the a time. How much of the original acid would need to be destroyed to go from pH 1 to pH 2, for this situation? 90%. From the start to pH 3, what would that percentage be? 99%. That means to go from pH 1 to pH 2, we had to get rid of 90%; it only required an additional 9% to get to the next pH unit. We could do a similar comparison between pHs 1 and 4 – to get to that point, you have to get rid of 99.9% of it, but that means from where you just came, pH 3, there's a change of only 0.9% compared to the original quantity. That means when we start out with the pH 1 solution, as we're adding sodium hydroxide, after this little initial part of the curve, the pH plateaus out – your adding hydroxide and adding hydroxide in slower, it slowly changes, until you've added 90% of the hydroxide you need, you've gone up one pH unit. Then you go just the next 9%, one tenth the distance you did before, it's gone up another pH unit. You go another one tenth and then another one tenth, and you'd get to where your volume's hardly changing, but the pH skyrockets. All I've done is to describe to you what happens with a log graph; when you graph things on a log scale, it make things non-linearly proportional. It is why we end up with this huge slope; it turns out that that occurs at the equivalence point. From that, we could get the volume of the equivalence point. We then can determine where we half the volume, because then that would be the half-equivalence point. At the half-equivalence point, that's exactly where the concentration of its acid is supposedly equal to its conjugate base concentration. When you have equal amounts of the acid and conjugate, then that's exactly when the pH equals the pKa. You do a titration; you find the volume needed to get to equivalence; you then find half that volume, look up the pH at that point, and that is the pKa, which is the point of reviewing what a titration was – to know how could we get the pKa of an acid through titration.

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The auto-ionization of water is an unfavorable process that does occur to some degree at any temperature since there will always be a fraction of molecules that have the energy to dissociate.

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$  at only one temperature. In pure water @ ???°C,  $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$

$pH \equiv -\log_{10} [H^+] = 7.00$  at only one temperature

$K_a = \frac{[H^+][A^-]}{[HA]}$  → acid dissociation constnat

If  $A=B$  (and acid/base conjugate pair)

An acid's strength ( $K_a$ ) is inversely proportional to its conjugate base's strength.

strong acid – extensive spontaneous dissociation →  $K_a$  large →  $pK_a$  small

$pK_a \equiv -\log_{10} K_a$

When solutions are highly concentrated, interactions between solute particles can cause deviations from predicted solution behavior → activity

Weak acids – acids that undergo only partial spontaneous dissociation

Given a 1.0 M of acetic acid (and ignoring activity), predict the pH of the sol'n.  $pK_a = 4.76$ ;  $K_a = 1.76 \times 10^{-5}$

If  $x \ll 1$ , the  $x$  can be ignored. 0.500 M acetic acid & 0.500 M sodium acetate;  $pH = ?$

This simplification only is valid if the concentrations of an acid and its conjugate do not shift substantially once the solution is prepared.

Titration

An indicator is chosen so that the  $pK_a$  of the indicator matches the anticipated pH of the titration sol'n at equivalence.

Equivalence point –  $n_{acid} = n_{base}$

Endpoint – The visual indication that a titration is complete (color change)

Neutral  $\equiv [H^+] = [OH^-]$

Neutralized  $\equiv n_{acid} = n_{base}$

If a weak acid (or base) is used in titration, the # of moles of  $H^+$  (or  $OH^-$ ) that are effectively generated will be less than the # of moles of acid (or base) itself.

∴ neutral ≠ neutralized

Once acetic acid is quantitatively neutralized by sodium hydroxide, a salt (sodium acetate) is produced that tries to re-establish equilibrium with the parent acid, acetic acid. To do this, acetate reacts with water, producing hydroxide, producing a basic solution.

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Structures – Identical to those from lab 11B (05/29/12)