

## Lecture 16A • 11/02/11

[lab report comments][calculation of percent composition in extraction lab][review for exam #2]

kinetics – RCD, rate limiting step, activation energy; reagents in a rate law are in the RLS

Sn2, it is a concerted, anionic mechanism. Because it's concerted, and because two molecules are involved at the same time in that rate-limiting step, that's why the 2 is in that name; it's bimolecular nucleophilic substitution. For Sn1, you're going to have at least two steps. All of the examples we've seen so far have had three, where first the bond breaks, you form a carbocation; so this is a step-wise, cationic mechanism. The second step, the most common example has been with water. Water starts out as neutral but becomes positively-charged when it forms a new bond; something has to give, and it's generally a hydrogen that comes off. Which of these three steps is the toughest? The first one, because it's a bond-breaking reaction that depends on forming a carbocation. Because there's only one molecule in that rate-limiting step, that's why this is a rate law with only one molecule in it, because only one molecule is in the rate-limiting step.

[RCD review – forward and reverse][Sn1 mechanism, Sn2 mechanism][hyperconjugation][stereochemistry – R/S, chiral/achiral; loss, retention, inversion of configuration, optical activity, racemic]

Nomenclature example

What's the most important thing on this molecule? –OH. Alcohol is more important than any hydrocarbon, which is more important than any halogen. The alcohol is most important; that automatically makes it position 1. We have to number sequentially one way or the other around the ring, [following] the first point of difference rule. Which direction's going to give us smaller numbers? We go counterclockwise or clockwise? Clockwise, so bromine's going to be at the 3 position.

Even before we finish this example, let's take something like this, to tackle how to number. How would we number that compound? Ethyl alphabetically shows up earlier than methyl, but that's not what necessarily makes us decide which way to number. Let's pick up a few scenarios. If I chose this methyl group over here and labeled it 1, then if I went clockwise, my next number I would run into is 3; if I went counterclockwise, the next number I would run into is 4. So out of those two directions, which would be the better one? The first one, because at the first point of difference, the first place as I'm going around the ring, three is lower than four, so I would go with three. But that's not the lowest possible set of numbers. If I had instead started with the methyl group and called it position 1, then I could have gone one way around the ring and gotten position three, or I go the other way around the ring and get position two. Since two is lower than three, that's a more correct way to do. But if I kept numbering around the ring, I would get 5; [1, 2, 5] would be my set of numbers. What if I chose one more way to number? What if I start with the ethyl group, not because 'e' in ethyl is lower than 'm' in methyl, but because if I give it the number 1, then if I go counterclockwise, the next position's two, and all the way over here, that's position four. It's not that 1+2+4 itself adds up to the lowest number; it's that, at each point along the ring, I've gotten the smallest number I can, starting with the first number. Everywhere, of course, the first number is going to be 1. Wherever you have a ring that has a substituent, if it only has one substituent, it is number one. But look at the first example: the next-lowest number I could get was only a three, but in either of these other two ways, the lowest number I could get was a 2. At that first point of comparison, that second substituent, since 2 is less than 3, I go with the 2. But then I have a choice: do I want [1, 2, 5] or [1, 2, 4]? Four is lower than five, so this bottom way is the correct way to number the ring. You only look at alphabetization if you can't decide which way; if two ways of numbering are identical, then you look at the names of the substituents.

Back to the one I wanted you to name. The top one, R or S? R. Oxygen is 1. The next positions over are equal, so we have to go to the next one out. Bromine's more important than carbon, so clockwise, so R. Bottom one: R. Bromine is importance number 1, then we have the two directions of the ring again. Again if I go out, the right side is more important to the left, it looks S, but it really is R because the least-important group is pointing at you. Functional group priority: out of any of the functional groups that's we've done any naming with, alcohols are more important; then you have alkenes and alkynes; then you have alkanes; then you have halogens. To finish off this name, we have the bromine, which would have the bromo- substituent name. So this would be 3-bromocyclohexanol. Notice I didn't put a number on the alcohol. Why? Because for rings, you leave the number out as long as it's obvious where that position is going to be. Since only one functional group is the important functional group – there's only one alcohol – you don't need to give the number. But we have stereocenters. If you only had one stereocenter, you don't use numbers with it. If you have multiple stereocenters, you must use numbers. When we're naming stereocenters, we go just in numerical order, so the first stereocenter's located at position one, the second position is 3, so this compound is (1R, 3R)-3-bromocyclohexanol. What if you had both R/S and E/Z? You just do it in numerical order.

[thermodynamics – state function; why is it important that enthalpy is a state function]

Here's a reaction coordinate diagram for a reaction. How many reagents are in the rate law for this reaction? Just because you see a diagram and know it's one step, you have no idea how many reagents are involved; you have to know what the mechanism is to come up with the number of reagents in the rate-limiting step. How would this change if I put in a catalyst? It lowers the activation energy. It does, yes, but not really, because it's a different reaction when you put a catalyst in. It could have multiple steps. It doesn't just lower the activation barrier, it gives a whole new reaction pathway. The activation barrier in that new reaction pathway is lower in energy than the original one, which if you're at the same temperature, and you're ignoring steric effects, then that means it's going to have a faster rate of reaction. Yes, the simple answer is lower activation energy, but [it's] more important to show that it's a different reaction path. A catalyst lowers the activation energy for a reaction by giving a new reaction pathway. But what happened to the energies of the products and reactants? They have to be the same, because Hess's law tells you that it doesn't matter how a reaction occurs, the enthalpy change just depends on the reactants and products. So what does a catalyst do to equilibrium? Doesn't do a thing. It lets you reach equilibrium more quickly, but it doesn't change equilibrium, because equilibrium depends on the energy difference between products and reactants, and if a catalyst doesn't change that, because of Hess's law, then a catalyst doesn't change K, a catalyst does not affect equilibrium.

[equilibrium – three definitions of concentration, rate, and energy; Le Châtelier's principle][delocalization and resonance structures; SMOG for allyl anion]

#### Acids and bases

How am I going to tie Le Châtelier's principle to acids and bases? What's a weak acid? What's delta G for the dissociation of a weak acid? Endergonic, which means that for a weak acid dissociation, you could draw a reaction progress diagram that looks like this. This is a likely reaction progress diagram for the dissociation of a weak acid. Why, because a weak acid is an acid that only minimally dissociates. We could take a generalized acid HA and show it splitting up in to H<sup>+</sup> and A<sup>-</sup>. That process we could write an equilibrium constant for, which we call K, which is products over reactants raise to their stoichiometric coefficients, which for a monoprotic acid mean[ing] one in which only one proton comes off, it's a pretty simple expression. If you don't get much dissociation, you don't get much products. If you don't get much products, K is small. K is mathematically linked, so if you have a small K, you have a positive free energy. Really tiny like less than one K, log of something less than one is a negative number. A negative of a negative number is a positive value; a positive delta G is an endergonic reaction, which means that equilibrium, it wants to lie mostly towards reactants, which means the acid doesn't want to dissociate.

What happens if we neutralize this with a strong base? If this a weak acid and we force it to react with the base, what's going to result? If I gave you an acidic solution made up of a weak acid and I take exactly the number moles of base needed to exactly neutralize that acid, what would the pH of the solution be? It can't be 7 because if you force this to completely dissociate, you are getting of all of the reactants and just making products. Your Q will be far past equilibrium. You you're sitting around in solution, then, with just this conjugate base, it's going to be reacting with anything it can, including the water in the solution if we're assuming an aqueous environment. It'll even react with that water so that it could go back down energetically to re-reach equilibrium. So if you have the dissociation of an acid that doesn't want to go that far, and you disturb the equilibrium by adding a base – that's the Le Châtelier's part – you force that proton off; you force it to become a product when it doesn't want to. Le Châtelier's principle says that it's going to go right back and respond to that stress, which means it's going to try to take a proton from wherever it can, including the solution it's in. When that happens, it's going to make the solution basic. This explains why acids and bases, they have their conjugate strengths the way they do because it's related to delta G.

What is neutral? Why can pH 7 not be defined as neutral? Because it depends on temperature. Why is pH 7 called neutral? Because of the autoionization of water, which means water breaking up to become H<sup>+</sup> and OH<sup>-</sup>. Is that a favorable reaction? Why does it happen? Because some of the molecules have enough energy to be able to disassociate. This is unfavorable, but some molecules have enough energy to dissociate. At room temperature, you get a concentration of exactly  $1.0 \times 10^{-7}$  M for H<sup>+</sup> concentration. We have this function pH, which is defined as the negative base ten log of the concentration of H<sup>+</sup>. In this case, it equals 7 for pure water at roughly 25 °C? What if we change temperature? We change the fraction of molecules that have that energy to dissociate, so you change the H<sup>+</sup> concentration. So pH 7 as neutral is only true at one temperature. We can't make a definition of neutral off of pH because pH is variable. Let's try another one.

What is the definition of neutral? When water dissociates, you make equal moles of H<sup>+</sup> and OH<sup>-</sup>; that right there is the definition of neutral: neutral is when the concentration of H<sup>+</sup> is equal to the concentration of OH<sup>-</sup>.

What is neutralized? It's not when the solution is neutral. It has nothing to do with H<sup>+</sup> and OH<sup>-</sup>; it's when moles of acid that you've added to the solution equal to moles base. The big question that we're going to use Le Châtelier's principle to explain is why is neutral not the same thing as neutralized. If you throw in equal moles of acid and base. Here's an acid and base; one mole of acid, one mole of base. They will neutralize, they will react. But if that base pulls off all of the protons of that weak acid, you've pushed the equilibrium of that weak acid all the way to the right, where it doesn't want to be. That equilibrium will try to shift back, reestablish equilibrium; the only way it has to do that is to pull protons back off whatever just removed them.

After you've added equal moles of acid and base, you don't have a complete reaction. Because that pullback is going to happen, because it tries to reestablish equilibrium, you won't have equal amounts of H<sup>+</sup> and OH<sup>-</sup>, so neutralized is not neutral.

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Kinetics: RCD, RLS, E<sub>a</sub> → The reagents in a rate law are in the RLS

Hyperconjugation; Stereochemistry – R/S; achiral/chiral; loss [S<sub>N</sub>1]/retention/inversion [S<sub>N</sub>2] of configuration; optical activity → racemic mixture

Thermodynamics – what it is a state function and why is it important that enthalpy is a state function.

A catalyst lowers the E<sub>a</sub> for a rxn by giving a new rxn pathway.

A catalyst does not change ΔH (or ΔG), since Hess's law states those values only depend on the identity of the products and reactants. Thus, a catalyst will not affect the balance of products and reactants in equilibrium

Equilibrium - 3 definitions ([ ], rate, E); Le Châtelier's principle

Delocalization and resonance structures

This is a likely RP diagram for the dissociation of a weak acid. Weak acid → an acid that only minimally dissociates.

neutral ≡ [H<sup>+</sup>] = [OH<sup>-</sup>]

Autoionization of water: H<sub>2</sub>O ⇌ H<sup>+</sup> + OH<sup>-</sup>

Unfavorable, but some molecules have enough energy to dissociate.

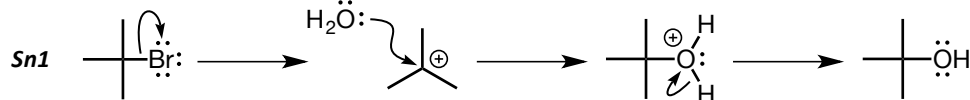
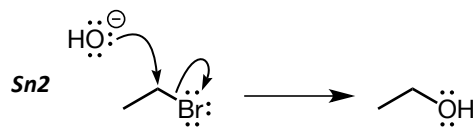
pH ≡ -log<sub>10</sub>[H<sup>+</sup>] = 7 for pure water @ 25 °C.

neutralized ≡ moles acid = moles base

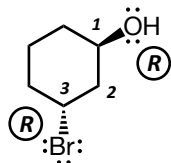
why is neutral ≠ neutralized

Structures

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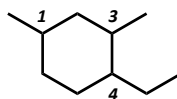


(1R, 3R)-3-bromocyclohexanol

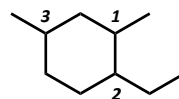
For only one stereocenter,  
numbers are not used; for  
multiple stereocenters, numbers must be used

# can be left out since most  
important functional group  
is automatically #1

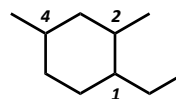
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[1, 3, 4]



[1, 2, 5]



[1, 2, 4]  
lowest set of #s

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