I believe a practical way to learn pK_a values is to do the following:

- **NOT use flashcards as your primary resource of learning.** Listen, I won't go so far as saying that flashcards have no place in organic chemistry education, but I will tell you from LOTS of experience that students who rely heavily on flashcards as their way of fooling themselves into thinking they are learning things like pK_a values, functional groups, and reactions are students who underperform and fail exams. Just saying.

- Have a resource that lists what the essential pK_a values are so you know what you need to know. These lists are everywhere, and I have created my version of it as well.

- Don't just memorize the values; make the effort to understand WHY the values are what they are relative to other compounds. For example, don't just memorize that methanol (CH_3OH) is a pK_a of about 16 while methylamine (CH_3NH_2) is a pK_a of about 35 . . . take the time to rationalize that a neutral sp^3 alcohol should be more acidic than a neutral sp^3 amine because of the periodic table trend that atoms from the same row become better at stabilizing a lone pair as you move to the right and become more electronegative.

- **You need to understand how to match a compound to an equivalent representation on a pK_a table.** *This comes down to recognizing functional groups.* For example, if you were asked about the pK_a of diethylamine [$(CH_3CH_2)_2NH$ – a neutral sp^3 hybridized nitrogen with one hydrogen and two alkyl groups], you would need to see that as roughly equivalent to ammonia with respect to using most pK_a tables. **An sp^3 alkyl group and a hydrogen are roughly equivalent to each other with respect to influencing acidity;** this is why water and methanol are about the same pK_a value.

- **Use practice drill sets to master the pK_a values.** It is important to see the different functional groups and learn to recognize them in the context of acid-base.

Never ceases to amaze me . . .

The one thing I BEG AND PLEAD for students to memorize is the essential pK_a values.

And yet, many just won't do it.

Students three quarters of the way through their first semester still cannot tell me that the pK_a of a carboxylic acid is about 5, or they try telling me the pK_a of water is 7.

But these same students make Herculean efforts to memorize mountains of shit that won't help them.

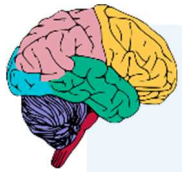
Using Practice Drill Sets to Learn pK_a Values

As mentioned on a previous slide, I believe a practical way to learn pK_a values is to work with pK_a practice drill sets. This is far more effective than trying to memorize a handout or flashcards. You should be able to find these types of drill sets easily online.

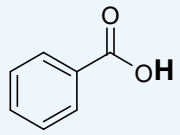
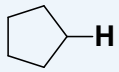
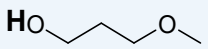
Learn the values in an "open-book" manner. Have a pK_a values reference chart by your side as you work on drill problems similar to what is shown below and refer to the chart when necessary.

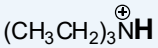
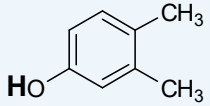
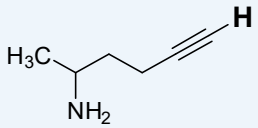
You will probably be surprised by how quickly you memorize the essential pK_a values when you do it this way because you will see there are only about 10 functional groups that are repeatedly featured in these types of problems. Part of your responsibility is to get accustomed to recognizing the functional groups involved, and this is one reason it is so much more effective to see new problems and various presentations of molecules instead of looking at the same static flashcards and handouts.

Some examples of the type of drills I'm talking about are shown below, so here's a chance for you to practice.



What are the pK_a values of the bolded hydrogens in each of the following compounds? Refer to your pK_a values reference chart as necessary.

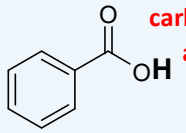
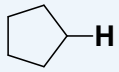
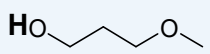
Compound	pK_a value
	
	
	

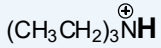
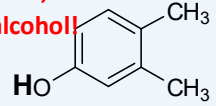
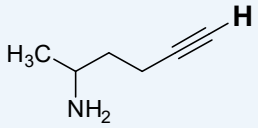
Compound	pK_a value
	
	
	

solutions on next slide

KEY: Using Practice Drill Sets to Learn pK_a Values

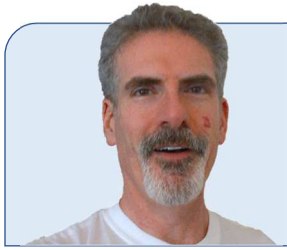
What are the pK_a values of the most acidic hydrogen in each of the following compounds? Refer to your pK_a values reference chart as necessary.

Compound	pK_a value
 carboxylic acid	5
alkane 	48-50
 alcohol	16

Compound	pK_a value
protonated sp^3 amine 	9
phenol, NOT alcohol! 	10
	25

Terminal alkyne is more acidic than a neutral sp^3 amine.

The Term pK_{aH} is Another Way of Saying "pK_a of the Conjugate Acid"



It will help a lot if you are aware that the term **pK_{aH}** is another way of saying "the pK_a of the conjugate acid". Now, there is a possibility you will not encounter the term pK_{aH} in your specific organic chemistry class, but this is a real term and a useful way of talking about the pK_a of the protonated form of a compound. **I will be using this term in our teachings; you will especially see the value of this concept when we discuss leaving groups.**

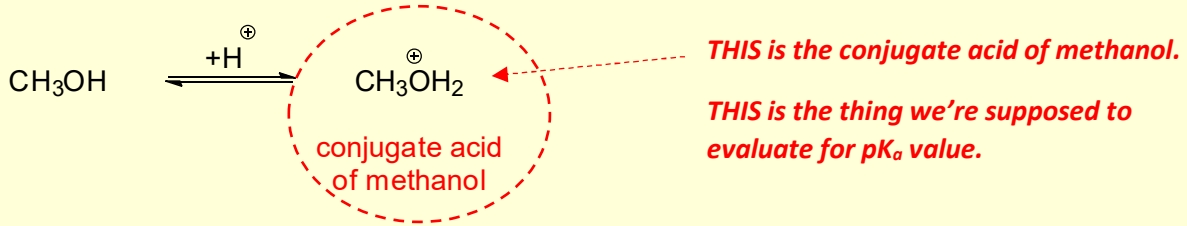
When you see the term pK_{aH} being used, it means add a hydrogen to the compound and then figure out the pK_a value of the protonated version of the functional group.

Probably the best way to illustrate this concept is through a simple example, so let's check it out.

Question: **What is the pK_{aH} value of methanol (the compound CH_3OH)?**

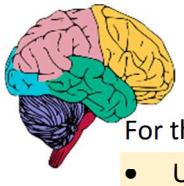
HINT: the correct answer is NOT any number between 15 and 19.

Answer: Methanol is the alcohol CH_3OH. The question is really asking, "What is the pK_a value of the conjugate acid of methanol?"



Asking, "What is the pK_{aH} of CH_3OH?" is really asking, "What is the pK_a of $CH_3OH_2^+$?"

Answer: The pK_a value of a protonated *sp*^{3} alcohol is about -2.

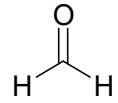
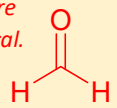
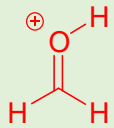
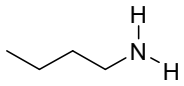
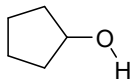
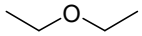
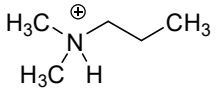
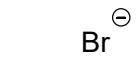


Drill Practice: pK_a and pK_{aH}

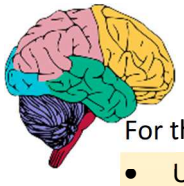
For the compounds shown below, fill in the chart accordingly.

- Under **"most acidic hydrogen"**, redraw the structure and indicate which hydrogen is determining your choice for the pK_a value you write. You may need to draw in the hydrogen if it isn't shown implicitly.
- Indicate the approximate pK_a value.
- Draw the structure of the conjugate acid being used to determine the pK_{aH} value.
- Indicate the approximate pK_{aH} value.
- ***Watch out for chicanery*** – there may not be a way to have a conjugate acid! Assume there is no possible conjugate acid if there is no lone pair on the structure. In other words, no lone pair = no pK_{aH} value!

The first line has been filled in for you to demonstrate what we're trying to do.

structure	most acidic hydrogen	pK_a value	conjugate acid for assessing pK_{aH}	pK_{aH} value
	*Either hydrogen is correct, they are identical.* 	**Around 44.** **Most similar to an *sp²* alkene hydrogen.**		**around -6** **(*sp²* oxonium ion)** **GREAT AWARENESS: hydrogen on oxygen cation has $pK_a < 0$.**
				
				
				
				
				

solutions on next slide



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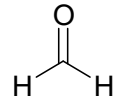
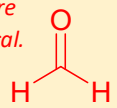
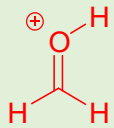
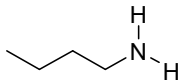
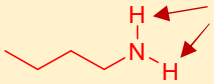
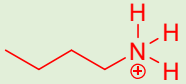
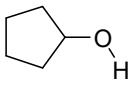
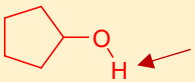
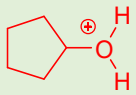
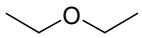
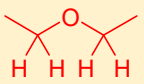
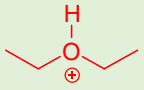
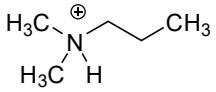
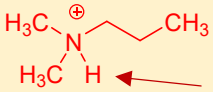
The first line has been filled in for you to demonstrate what we're trying to do.

structure	most acidic hydrogen	pK_a value	conjugate acid for assessing pK_{aH}	pK_{aH} value
	*Either hydrogen is correct, they are identical.* 	**Around 44.** **Most similar to an *sp²* alkene hydrogen.**		**around -6** **(*sp²* oxonium ion)** **GREAT AWARENESS: hydrogen on oxygen cation has $pK_a < 0$.**
	 *either one*	**around 35** **(*sp³* amine)**		**around 9** **(protonated *sp³* amine)**
		**around 16** **(*sp³* alcohol)**		**around -2** **(*sp³* oxonium ion)**
	 *one of the 4 next to oxygen*	**around 50** **(*most similar to an alkane hydrogen*)**		**around -2** **(*sp³* oxonium ion)**
		**around 9** **(protonated *sp³* amine)**	**none: no lone pair**	**none**
	**none: no hydrogen**	**none**	H—Br	**-9**