Frequently asked Questions and Answers on the Acid and Base strength
CH101/2 General Chemistry, Boston University, January 17, 2007

1. First, it is important to be precise in terminology. In the equation

$$\textbf{H-Ac} + \textbf{:OH}_2 <=> \textbf{H-OH}_2^+ + \textbf{:Ac}^-$$

there are two base-conjugate acid pairs. $:Ac^-$ is a base and H-Ac is its conjugate acid; $:OH_2$ is a base and $H\text{-}OH_2^+$ is its conjugate acid. This allows us to see, in response to your question "If you mixed $H(C_2H_3O_2)$ (H-Ac?) with $:OH_2$, would the Lewis base be the acetate ion?", that in every acid-base equation there are always two acids and two bases, as conjugate pairs.

Finally, in deciding on strength, it is always *relative* to something else. For example, we may ask which is the stronger base, $:OH_2$ or $:Ac^-$? One way to answer this is to see what happens when we add each base to water. We know that adding $:Ac^-$ to water results in a pH > 7, a basic solution, whereas if we add water to water (!), the result is a pH = 7. This means that in the competition for H^+ to form the conjugate acid, :Ac- wins out over $:OH_2$. That is

$$\textbf{H-OH} + \textbf{:Ac}^- \textbf{(base)} <=> \textbf{H-Ac (conjugate acid)} + \textbf{:OH}^-$$

is more to the product side than

$$\textbf{H-OH} + \textbf{:OH}_2 \textbf{(base)} <=> \textbf{H-OH}_2^+ \textbf{(conjugate acid)} + \textbf{OH}^-$$

In this way we see that the H-Ac bond is stronger than the $H\text{-}OH_2^+$ bond, and so we conclude the following (as shown in Table 6.2 on page 370): (1) H-Ac is a weaker acid (stronger bond means H^+ is less available) than $H\text{-}OH_2^+$. (2) $:Ac^-$ is a stronger base than $:OH_2$.

2. Say we have a strong Lewis base, $:S^-$, and a weak Lewis base, $:W^-$, and that each is able to bind a proton to form their conjugate acid, H-S and H-W.
Because $:S^-$ is a strong base, the H-S bond in its conjugate acid will be strong and so in aqueous solution there will be an appreciable amount of H-S compared to $:S^-$. That is, we can expect the aqueous acid-base equation to be shifted toward reactants at equilibrium.

$$\textbf{H-S} + \textbf{:OH}_2 <=> \textbf{H-OH}_2^+ + \textbf{:S}^-$$

Because: W^- is a weak base, the H-W bond in its conjugate acid will be weak and so in aqueous solution there will relatively little H-W compared to: W^-. That is, we can expect the aqueous acid-base equation to be shifted toward products at equilibrium.

$$\textbf{H-W} + \textbf{:OH}_2 <=> \textbf{H-OH}_2^+ + \textbf{:W}^-$$

Comparing these two equations, we can see that in the competition for protons, the weaker base, $:W^-$, is not as effective as $:S^-$, and so $:W^-$ predominates in solution over the stronger base, $:S^-$.

3. Student question: Question 6.20, it asks us to pick which of the pair would be the stronger base. I was under the impression that the element with the lower electronegativity would be associated with the stronger base. However for a) NH_3 is listed as the answer even though P has a lower EN which would make PH_3 the stronger base. The same thing again happens in d) where CH_3O is listed as stronger but S would have a lower EN so shouldn't CH_3S be the stronger base?

Professors Answer: Electronegativity is only one factor. P is BIGGER than N which allows the electrons in the lone pair to be more delocalized, stabilizing the base and making PH_3 weaker. Similarly S is bigger than O

4. HCN is a weak acid, but it is strong compared to water. This means that HCN will contribute some of its protons *to* water,

$H\text{-}CN + :OH_2 <=> H\text{-}OH_2^+ + :CN^-$

with the result that solutions of HCN will be acidic relative to pure water. Since HCN is a weak acid, $:CN^-$ is a strong base compared to water, and so it will take some of the protons *from* water,

$H\text{-}OH + :CN^- <=> H\text{-}CN + :OH^-$

with the result that solutions of $:CN^-$ (such a NaCN), will be basic relative to pure water.

5. In lecture professor asked which one was more acidic HOCl or HOBr. The answer that was given was HOCl because Cl is more electronegative than Br so it would pull the electrons closer away from oxygen thereby weakening the OH bond thus making it more likely to donate the hydrogen.

This is correct.

This is exactly the kind of thing we want you to consider when ranking a group of bases in order of increasing or decreasing basicity. We learned that size and electronegativity play a part in determining the basicity of a molecule. However, as in this case, sometimes it's hard to tell what "wins" out, size or electronegativity. Your textbook emphasizes the relationship between size and stability by using the halides as an example. I^-, being larger and more stable, is a weaker base than F^-. HClO and HBrO are different beasts all together, and I commend your thoughtfulness in reasoning that BrO^- is a weaker base. What's key here is the attachment site of the H^+ ion. In the textbook example, the H^+ ion attaches directly to the halide ion, and so the size and stability of the halide ion is crucial. In BrO^- and ClO^- the attachment of H^+ is on the oxygen atom in both cases; the size of the halogen is not as important now. What *is* important is the effect the electronegativity of the halogen has on the oxygen atom. I hope this sheds some light on your confusion.