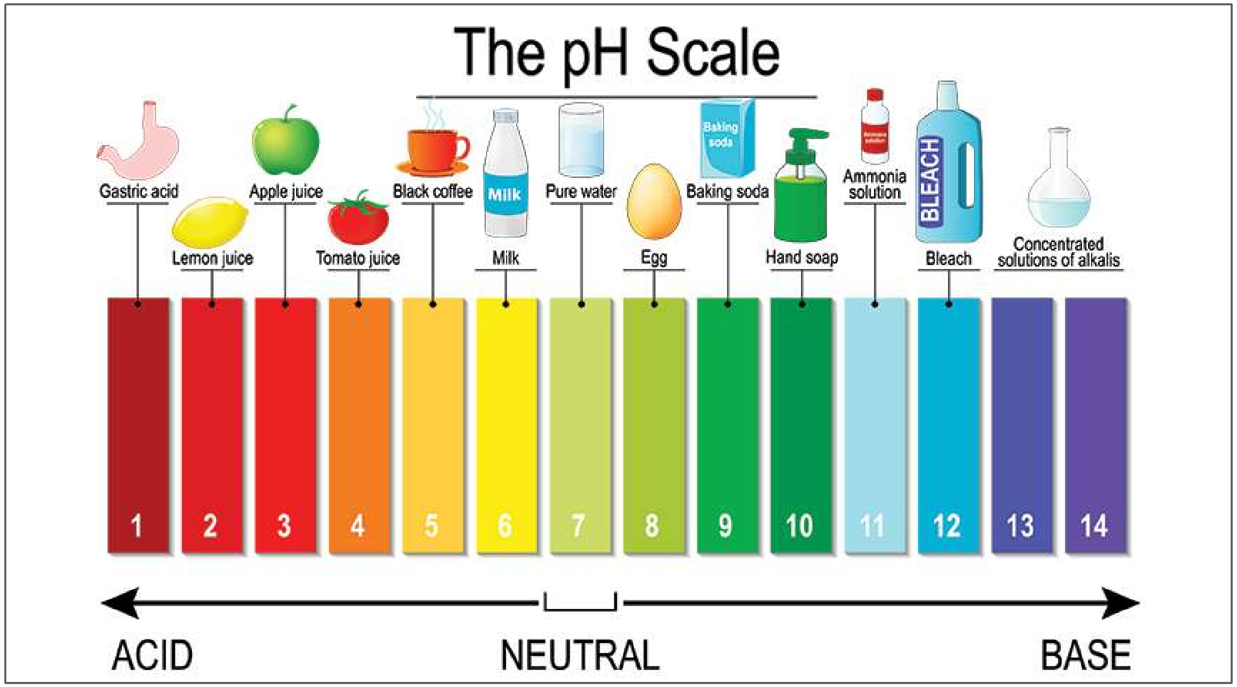
Chapter 3 NOTES

Acids and Bases

Organic Chemistry

Adapted from David Klein's Organic Chemistry as a Second Language

---



3.0 Introduction to Acids and Bases

There are three definitions that can be used to describe acids and bases.

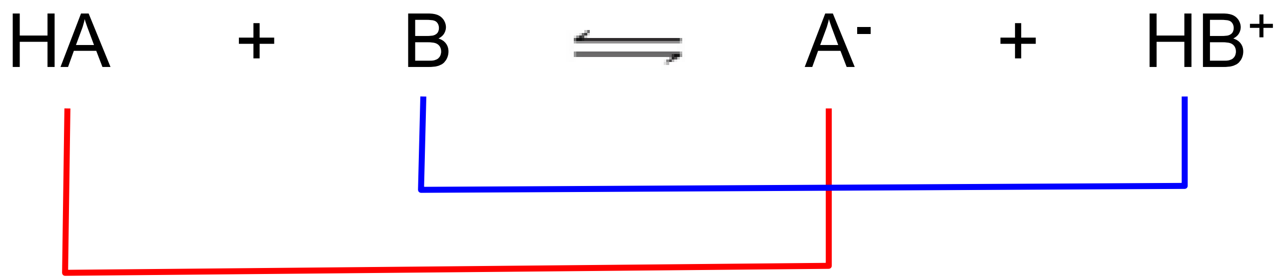
1. **Arrhenius A-B Theory:**
   - Acids: create H^+ as a product
     (H^+ is really H_3O^+ which we call hydronium ion)
   - Bases: creates OH^- as a product (hydroxide ion)

1. **Bronsted-Lowry A-B Theory:**
   - Acids: donate H^+ (we call it a proton but remember it's H_3O^+)
   - Bases: accepts H^+
     - Theory we primarily use, uses conjugate acid-base pairs

1. **Lewis A-B Theory:** **forms a new molecule**
   - Acids: accept an electron pair (to form a covalent bond)
   - Bases: donates an electron pair (to form a covalent bond)

3.0 More about Bronsted-Lowry Acids and Bases

- **Brønsted-Lowry definition**
  - Acids donate a proton (H^+)
  - Bases accept a proton (H^+)
- In Gen Chem, we usually use symbols to represent the different parts of the chemical reaction:



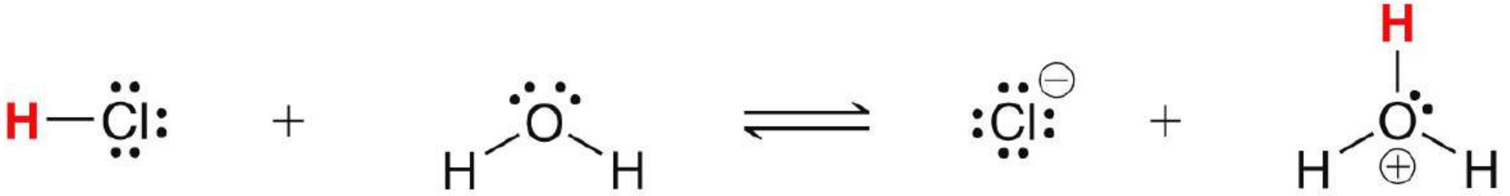
$$HA + B \rightleftharpoons A^- + HB^+$$

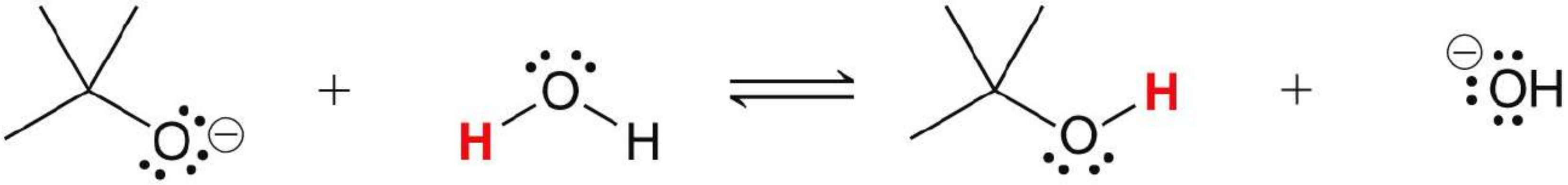
Conjugate Acid-Base Pairs: These are the two “species” that are formed on each side of the chemical reaction.

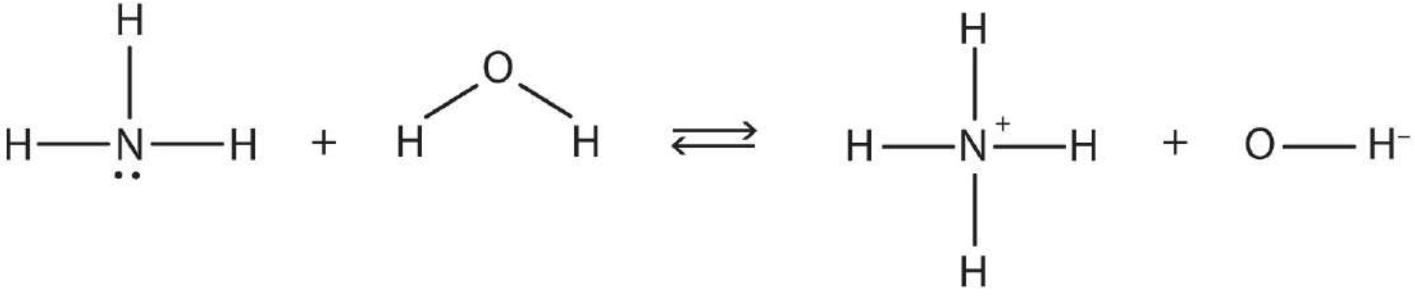
HA = the acid and A^- = it’s conjugate base
B = the base and HB^+ = it’s conjugate acid

Ch 3.0: Intro to A-B Theories

Practice Labeling Acids, Bases, and Conjugates
*Connect the A-B Pairs

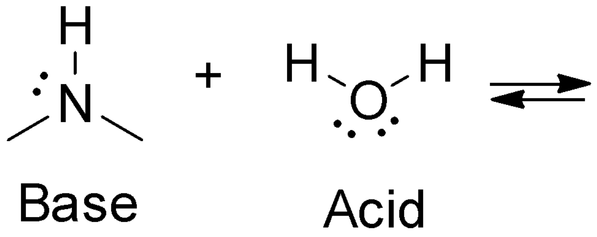


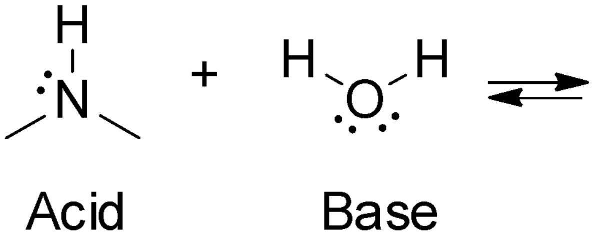




Practice Predicting the Products

Draw reasonable products for the following acid/base reaction, and label the conjugates.

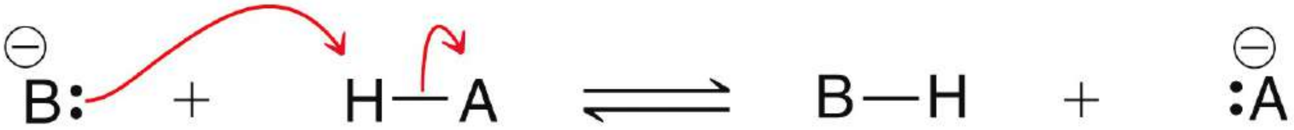




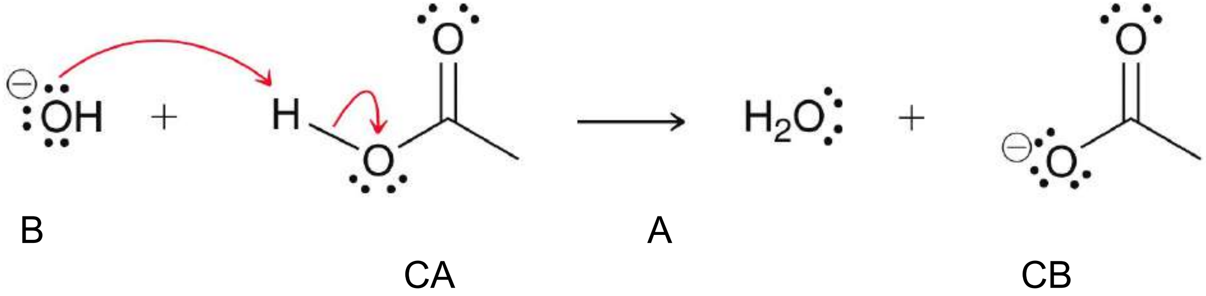
Water is was able to act as an acid OR and base, this means it is ***amphoteric***

Curved Arrows in Reactions

- When bonds break and form, **pairs of electrons** move, and we can show their movement with curved arrows
- Consider the following generic acid/base reaction



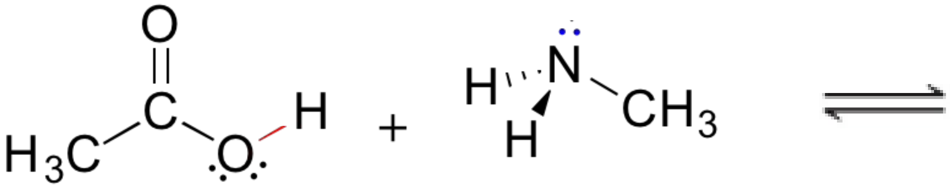
- How are the curved arrows here different from the ones we use to represent resonance in chapter 2?
- The curved arrows show the reaction **mechanism**
    - drawing **mechanisms** is one of the most valuable skills in o-chem



- You could say the base “attacks” the acid
- *The acid cannot lose its proton without the base taking it. All acid/base reactions occur in one step. The mechanism shows two arrows indicating*

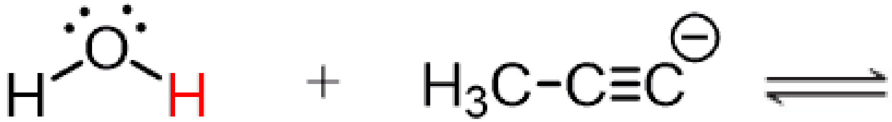
Curved Arrows in Reactions Practice

Predict the products and draw curved arrows for the following acid base reaction mechanism. Label the A, B, CA, and CB while connecting the pairs



H-A
acid

:B
base



acid

base

Ch 3.0: Intro to A-B Theories

3.1 - 3.4 *Quantifying Basicity using ARIO*

- Recall from General Chemistry, how do “strong” acids/bases differ from “weak” acids/bases?
  - Strong bases will “push” the reaction away from them
    - remember that molecules “*want to become stable*” and they will proceed with the reaction that creates a **more stable product**

There are 2 ways you can determine the strength of a base:

- We will learn to do **Qualitative** strength analysis (sections 3.1-3.5) – comparing the general stability of molecule structures.
  - specifically we will use the ARIO method of analysis for each base

- We will learn to do **Quantitative** strength analysis (section 3.6)– using pK_a values to compare the strengths of acids

Qualifying Basicity

- **Qualitative analysis** – compare structural stability to determine which is a more stable base
  - Formal charge can affect stability
    - The more effectively a reaction product can stabilize its formal charge, the more the equilibrium will favor that product
  - *The more effectively a conjugate base can stabilize its negative charge, the stronger the acid it was that the base was created from*

- What factors affect the stability of a negative formal charge?
  - The type of **Atom** that carries the charge
  - **Resonance**
  - **Induction**
  - The type of **Orbital** where the charge resides

These factors can be remembered with the acronym, **ARIO**

You will have to draw the potential products for each H that could be removed. It is very simple. Remove the H and put on a negative charge!

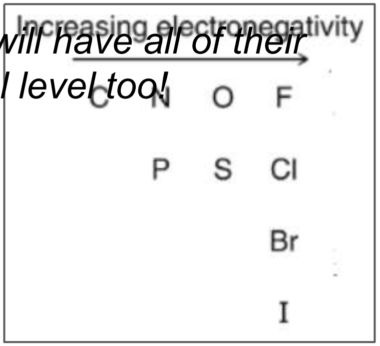
Factor 1: The Atom

- **A**RIO - The type of **atom** that carries the charge

Elements in the same row

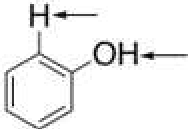
If the elements are in the same row, the more electronegative atom will be more stable.

- *Remember electronegativity is the measure of an atom's ability to attract electrons. So it makes sense that the more electronegative atom will be better at stabilizing a negative charge.*
- *The atom in the same row will have all of their electrons in the same orbital level too!*



Example:

Determine which H will be more acidic. Draw both possible conjugate bases.

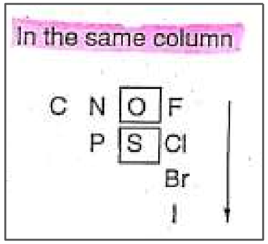


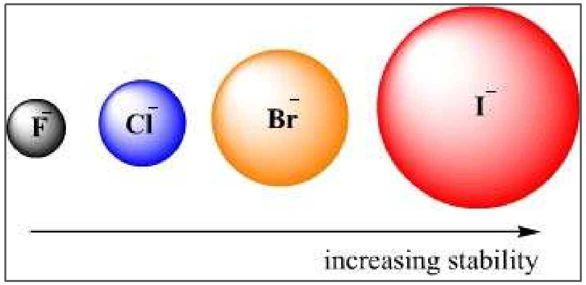
conjugate base #1 conjugate
base #2

Elements in the same column

If the elements are in the same column, the larger atom will be more stable.

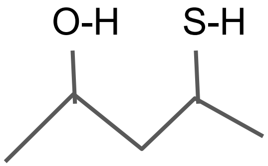
- *Larger atom size allows the charge to be spread over a bigger volume of space (not isolated as much)*
- *The stability difference between F^- and I^- is much less than that of C^- and F^- because electronegativity is a greater effect.*





Example:

Determine which H will be more acidic. Draw both possible conjugate bases.



conjugate base #1 conjugate
base #2

Ch 3.1: Factor 1 - The Atom

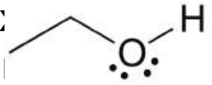
Factor 2: Resonance

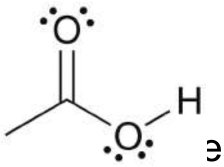
What happens when the atom the charge is on is the same? We go onto the next factor!

- ARIO - **Resonance** can greatly stabilize a formal negative charge by spreading it out into partial charges
    - *more resonance possibilities = more stable charge*
    - delocalized: the charge can be spread out over multiple atoms
        - the more delocalized the better!
        - however, resonance with 1 oxygen is better than with many C’s
    - localized: the charge is “stuck” on an atom

E

D


Ethanol


Acetic acid

es. Determine which compound will be more acidic. Explain your

re

Conjugate Base of Ethanol

Conjugate Base of Acetic Acid

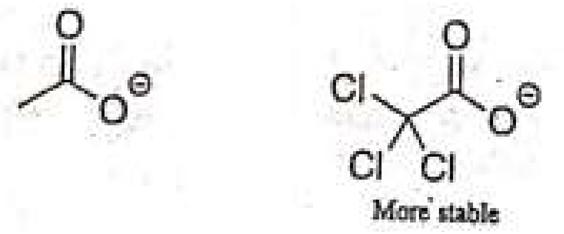
Explanation:

Ch 3.2: Factor 2 - Resonance

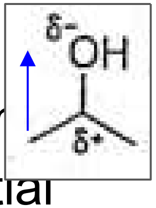
Factor 3: Induction

What happens when the resonance possibilities are the same? We go onto the next factor!

- ARIO - **Induction** can also stabilize a formal negative charge by spreading it out. A neighboring electronegative atom "pulls" on the electrons and helps to distribute the charge.



The Cl's are helping to pull some of the negative charge away from the oxygens. This helps to stabilize the charge.

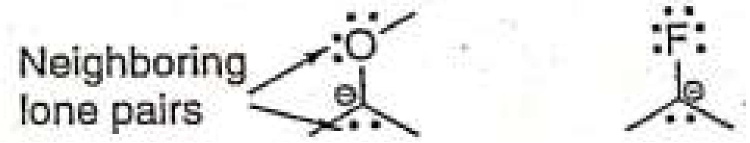


  - WHY does this work? Think back to when we studied polar molecules in Chem. We would draw a dipole with a partial positive charge and a partial negative charge. We thought of the δ- as "pulling" on the electrons
  - We need the electronegative atoms in the "Goldilocks" zone. You don't want the electronegative atoms *too close* or *too far away*

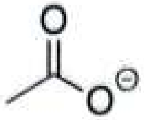
The Cl's here are an additional atom farther away from the charged atom so they don't have much effect towards stabilizing the charge.

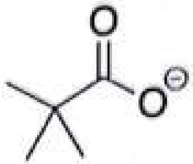
Ch 3.3: Factor 3 - Induction

- ARIO - Induction: Things that can "go wrong" for induction
  - **Alpha effect:** neighboring lone pairs on atoms can introduce more negative/repulsive effects that are destabilizing.

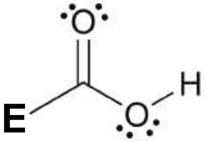


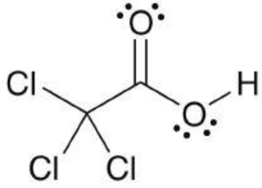
  - **Alkyl groups:** these neighboring carbons are electron donating, again these "push" electron ive charge that cause a destabilizing effect.


More stable


Less stable
Alkyl groups destabilize this negative charge

This destabilizing effect is really due to something called **hyperconjugation** - and it is *WAY* beyond the score of this course!


Acetic acid


Trichloroacetic acid

E

D ses. Determine which compound will be more acidic. Explain your

re

Conjugate Base of Acetic Acid

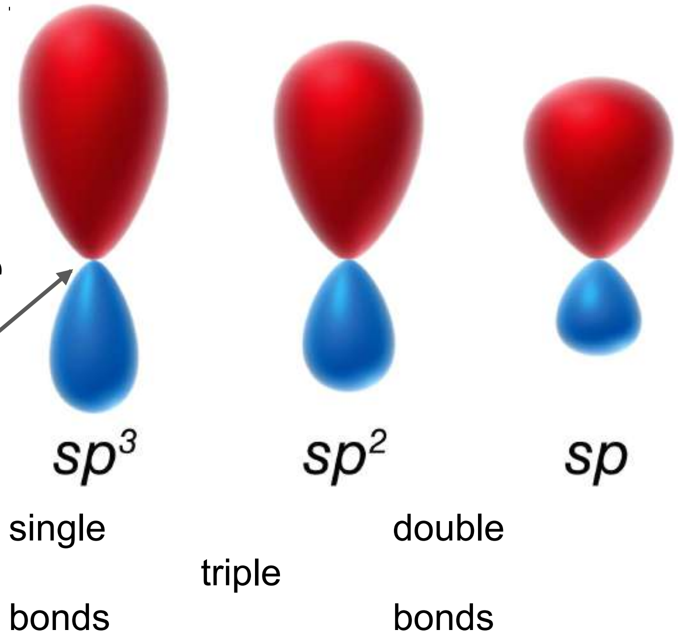
Conjugate Base of Trichloroacetic Acid

Explanation:

Factor 4: Orbitals

What happens when induction isn’t a consideration? We go onto the next factor!

- ARI**O** - The type of **orbital** also can affect the stability of a formal negative charge
- A negative charge is more stable if it is held closely to an atom’s nucleus. WHY?
    - Remember that opposite charges attract. The nucleus is positively charged because of the protons in it - so the electrons for the negative charge are stabilized when they are closer
        - single bonds are the longest
        - double bonds a little shorter
        - triple bonds are the shortest *(most able*

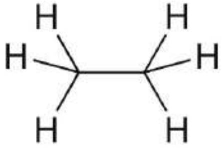


The nucleus would be located where the two lobes meet.

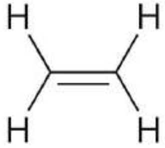
Ch 3.4: Factor 4-Orbitals

- ARIO - The type of **orbital** practice:

1. *Draw the conjugate base of each structure and determine which acid would be the most acidic.*



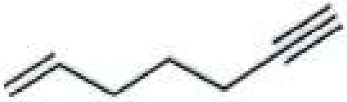
Ethane

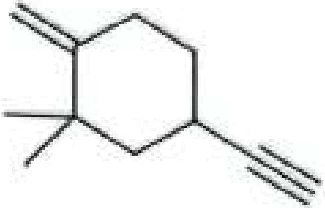


Ethylene

Acetylene

1. *t acidic proton in the compounds*





Ch 3.4: Factor 4-Orbitals Practice

IMPORTANT EXCEPTION FOR ARIO

Usually we go through all of the 4 factors in the order they were presented. But there is one important exception!

Compare these two acidic compounds (draw their CB's)

______________ ______________

We have two conflicting factors - the **Atom** and **Orbitals**.

According to the ARIO rules for Factor 1, the atom, N should be more stable with a negative charge compared to the C. However, factor 4, the orbital, actually "wins" because it has a greater effect of stabilizing the charge. This is an important exception to our ARIO order.

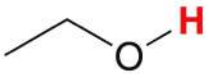
*Takeaway: when comparing a triple bond C- to a N-, the carbon will be more stable!

Ch 3.4: Factor 4-Orbitals

3.5 - Ranking the Four Factors

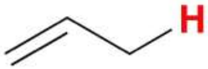
- When assessing the acidity of protons, we generally use **ARIO** as our order of priority
  1. The type of **atom** that carries the charge
  2. **Resonance**
  3. **Induction**
  4. The type of **orbital** where the charge resides *(Watch out for 3x bond C and N!)*

- Compare ethanol and propylene. Which has a more stable conjugate base? WHY?



Ethanol

pK_a = 16



Propylene

pK_a = 43

Complete the practice problems in sections 3.1 - 3.5 in the Klein Problem Packet through page 70 ***(if you have not already done so!)***

3.6 - Quantitative Measurement (pKa Values)

- ARIO is a good general guideline, but it sometimes fails
  - To determine the actual acidities, the pKa values must be experimentally measured and compared
  - Using the **pKa** values, you can never go wrong.
  - **The direction of equilibrium will shift away from the strongest acid (or towards the most-stable base depending on how you think about it.)**

Review from General Chemistry of K_a and pK_a

- K_a is the equilibrium constant for the reaction between an

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

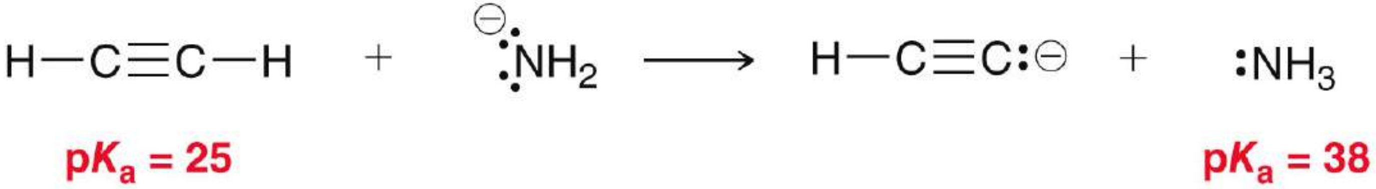
$$pK_a = -\log K_a$$

- K_a values range from 10^{-50} to 10^{10}
- Such very small and large numbers can be difficult to imagine
- If you take the -log of the K_a, that will focus you on the exponent of the

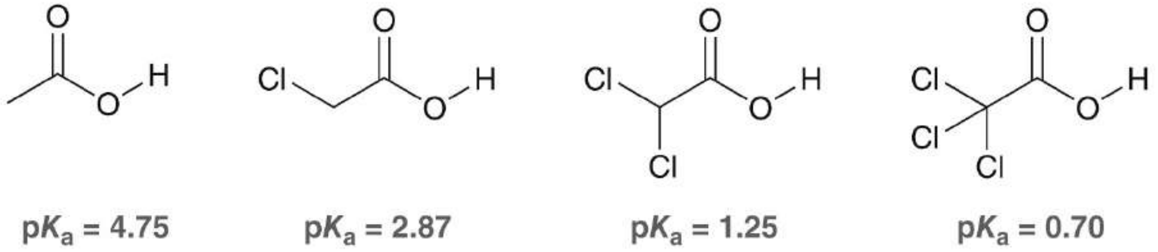
How to Use pKa Values

- **Strong acids** will have a **lower** pK_a value.
  - compare this to the concept of pH: the lower the pH, the stronger the acid
  - <u>For example:</u> a pKa of 4 for an acid means the proton is 1000x more acidic than a pKa of 7 because the logarithm is a base-10 calculation. 7 - 4 = 3 so 10 x 10 x 10 = 1000

Ex: Given the pKa values for the acids on each side of the equation, which acid is stronger? Which way do you think the equilibrium will shift?



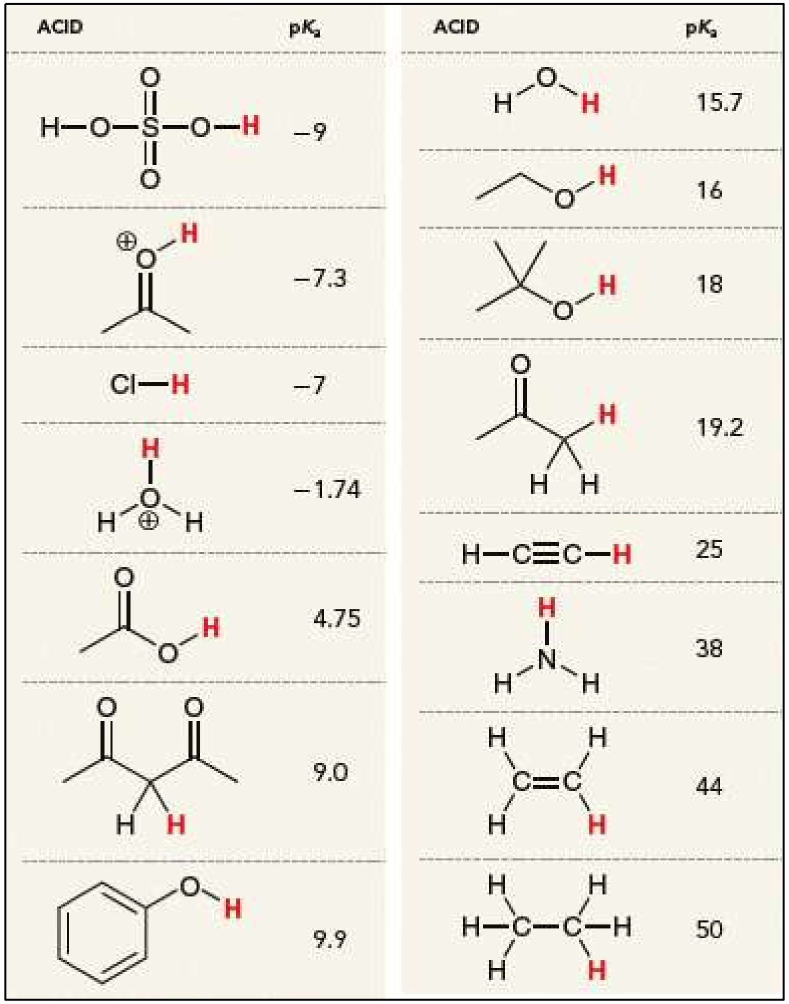
Ex: Use the concept of induction to explain the pKa values below



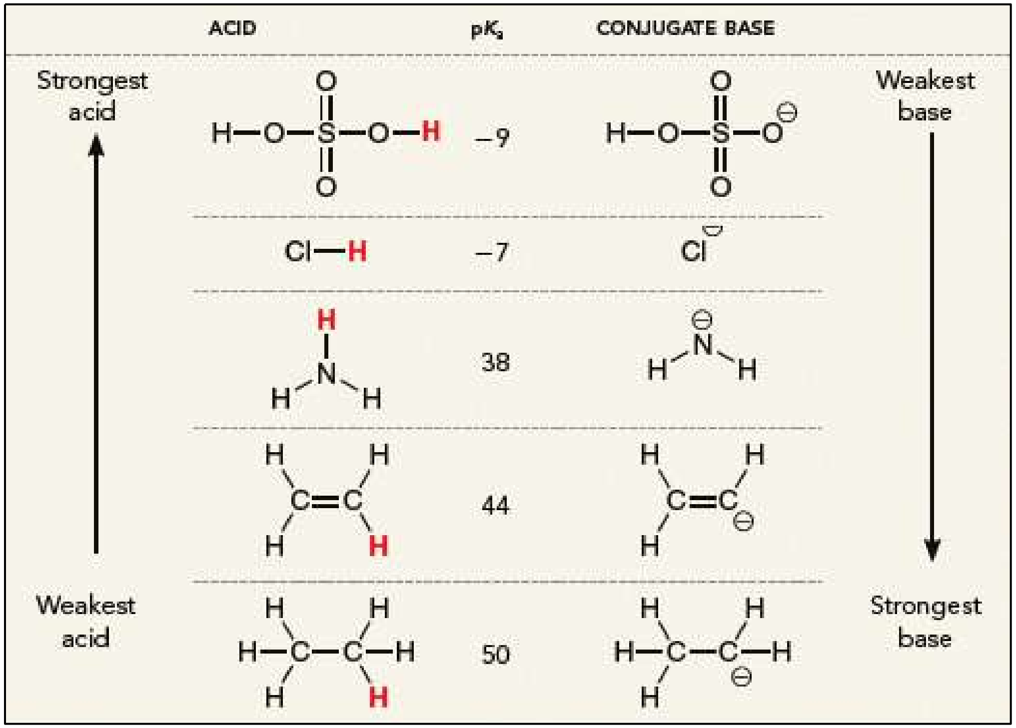
Ch 3.6: Quantitative Analysis: pKa Values

pKa and Acid/Base Strength

- You can also use pK_a values to compare the strengths of bases
- BELOW: Notice that the stronger the acid is, the weaker its conjugate base will be. *WHY?*
- SIDE: Use ARIO to explain the differences in acid strength.



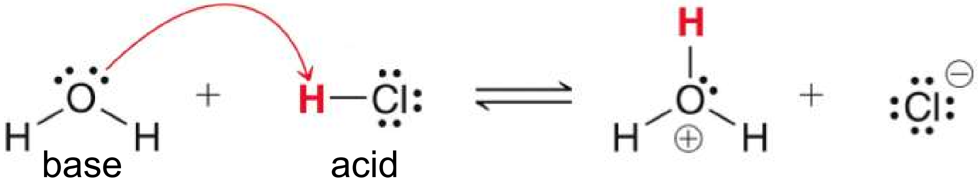
You will often be given a similar chart for pKa values. Sometimes you have to memorize specific ones in college.



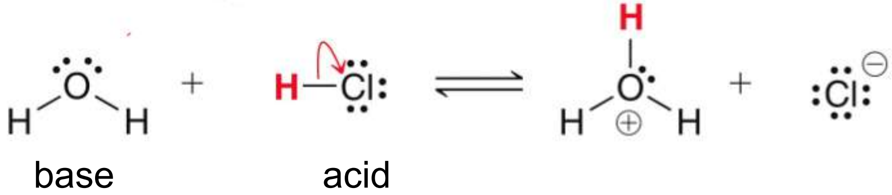
Ch 3.6: Quantitative Analysis: pKa Values

3.7 & 3.8 - Predicting Equilibrium and Showing Mechanisms

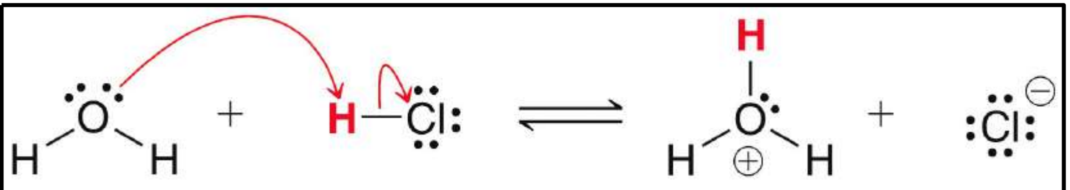
- Equilibrium will shift towards the more stable products. *(away from the "stronger" acids)*
- Mechanisms are the arrows used to show how the reaction occurred. For these acid-base reactions you will always have TWO arrows
  - similar to resonance arrows. The tail shows where the electrons "come from", the head where the electrons are "going".
  - We ARE allowed to break single bonds - because we are showing how the reaction occurred!
    - Arrow #1: Think of the base reaching out and grabbing the H+ from the acid.



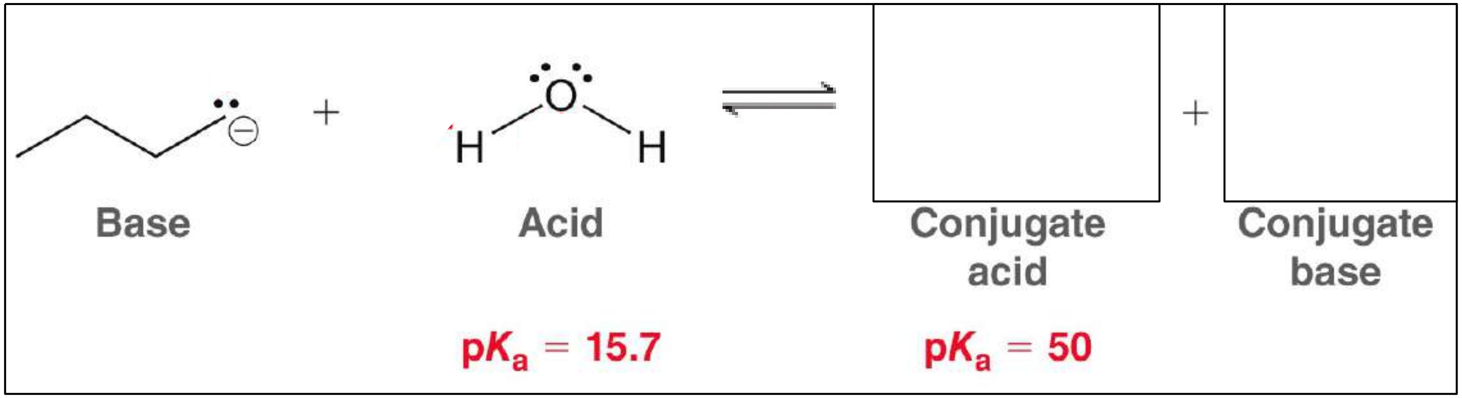
    - Arrow #2: The bon will then go back to the acid.

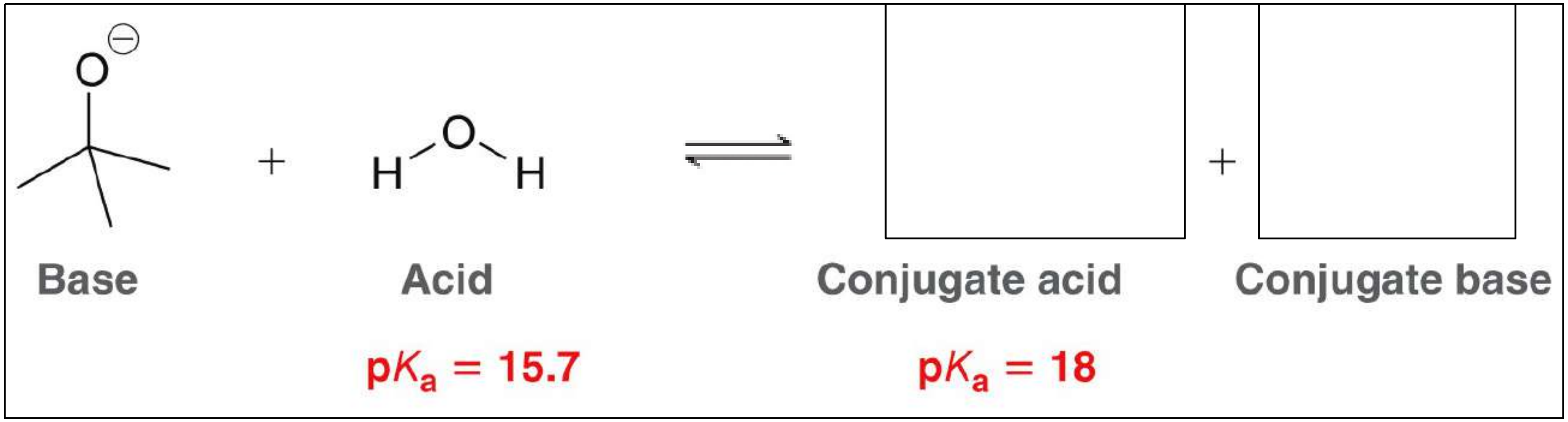


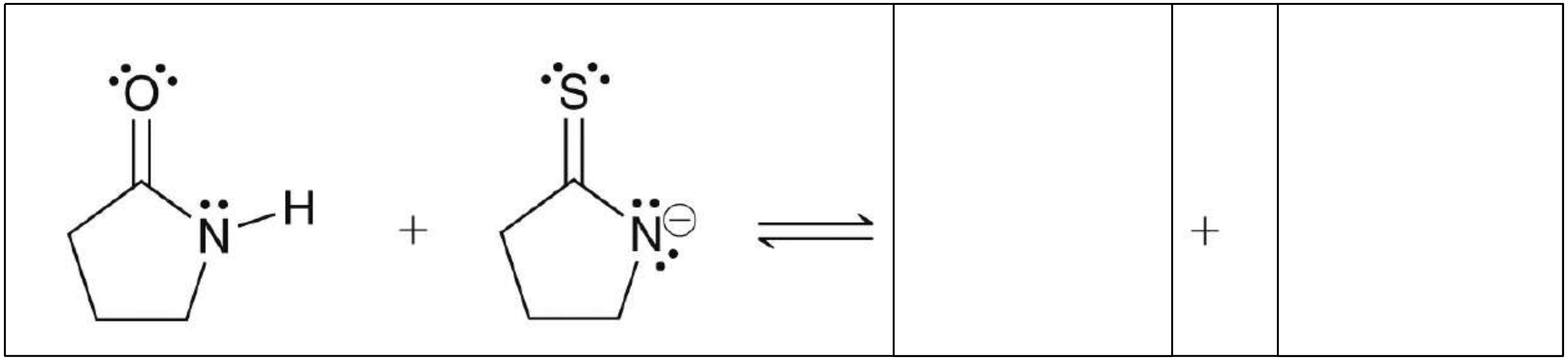
Put it all together



Additional Practice Problems: Draw the Mechanism, predict products, label parts, predict equilibrium shift







Topics for Ch 3 Test

① explain function of Acid + Base under Brønsted-Lowry def. (what we have used)

② explain how to determine strength of acid by looking @ its C.B.

③ label A, B, CA, CB

④ list out <u>ARIO</u> + explain each part (look @ "foldable")

⑤ Compare 2 acids + determine which would be stronger by looking @ their C.B.'s

⑥ Know general idea of pKa values (what a "stronger" one is when comparing)

⑦ draw 3 orbitals + label w/ hybridization

⑧ -show the mechanism (arrows)
 -draw products
 -label A, B, CA, CB
 -predict direction of equilibrium AND justify (explain your choice!)

⑨ Make sure you know "good" + "bad" inductive effects
↳ be able to explain the alpha effect!
"good" = stabalizing
"bad" = destabalizing