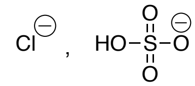
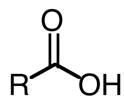
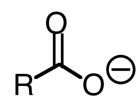
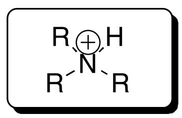
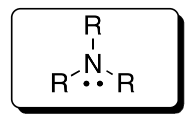
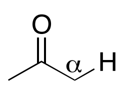
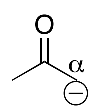
Acid-Base Chemistry (Section 1-12-14)

Acidity/Basicity Table

Entry	Class	Structure	Ka	Acid Strength	Base	Base Strength
1	Strong Acids	H-Cl, H_2SO_4	10^{2}			
2	Hydronium	H_3O^+, ROH^+ cationic	10^{0}		H_2O, HOR neutral	
3	Carboxylic Acid		10^{-5}			
4	Ammonium Ion (Charged)	 Charged, but only weakly acidic!	10^{-12}		 Neutral, but basic!	
5	Water	HOH	10^{-16}		$HO^{\ominus}$	
6	Alcohol	ROH	10^{-17}		$RO^{\ominus}$	
7	Ketones and Aldehydes		10^{-20}			
8	Amine (N-H)	$(iPr)_2N$-H	10^{-33}		$(iPr)_2N^{\ominus}Li^{\oplus}$	
9	Alkane (C-H)	RCH_3	10^{-50}		$RCH_2^{\ominus}$	

Quick Checklist of Acid/Base Factors
1. Charge
2. **Electronegativity**
3. **Resonance/Conjugation**
4. Hybridization
5. Impact of Electron Donors/Withdrawers
6. Amines/Ammoniums

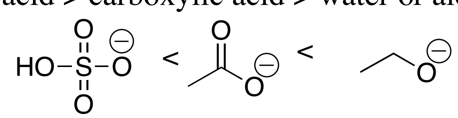
- **When a neutral acids are involved, it's best to draw the conjugate anionic bases, and then think from the anion stability side.**

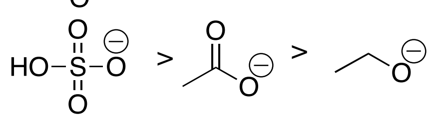
More Detailed Discussion of Acid/Base Patterns/Factors to remember

1. Charge: all else equal, cations are more acidic than neutrals, and anions more basic than neutrals.

2. Electronegativity:
   - Acidity: H-X (halogen) > H-O > H-N > H-C
   - Basicity: $X^{\ominus} < O^{\ominus} < N^{\ominus} < C^{\ominus}$
   - Anion Stability: $X^{\ominus} > O^{\ominus} > N^{\ominus} > C^{\ominus}$
   - Why: **The more stable the anion Z^- that forms, the more acidic the parent H-Z will be**. All acids H-Z must give up H^+. The better off the resulting anion Z^- is, the more willing H-Z will be to sacrifice H^+.
   - **The anion stability directly correlates the love for electrons.**
   - Notice three things:
     - ANION STABILITY and the ACIDITY OF A NEUTRAL ACID PRECURSOR ARE DIRECTLY RELATED.
     - ANION STABILITY and the BASICITY OF THE ANION ARE INVERSELY RELATED (more stable anion, less basic anion)
     - ANION BASICITY AND THE ACIDITY OF THE CONJUGATE ACID ARE INVERSELY RELATED (the stronger the acidity of the parent acid, the weaker the basicity of the conjugate anion)
   - KEY: WHEN THINKING ABOUT ACIDITY AND BASICITY, FOCUS ON THE ANION. THE STABILITY OF THE ANION DETERMINES ACID/BASE BEHAVIOR.

3. Resonance/Conjugation: Since anion resonance is stabilizing, **an acid that gives a resonance-stabilized anion is more acidic.** And an anion that forms with resonance will be more stable and less basic.
   - Oxygen Series Examples:
     Acidity: sulfuric acid > carboxylic acid > water or alcohol

     Anion Basicity: 

     Anion Stability: 

   - Note: Resonance is often useful as a tiebreaker (for example, molecules in which both have O-H bonds and both have equal charge, so that neither the charge factor nor the electronegativity factor could predict acidity/basicity)
   - NOTE: Resonance can sometimes (not always) trump electronegativity or even charge.
     - Example of resonance versus charge: A carboxylate anion, with serious resonance stabilization, ends up being so stabilized that it is even less basic than a neutral, uncharged amine! A hydrogen sulfate anion from sulfuric acid is less basic than not only neutral amines but also neutral oxygen (water, etc.)

4. Hybridization: For lone-pair basicity, (all else being equal), $sp^3 > sp^2 > sp > p$

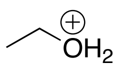
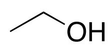
5. Electron donating/electron withdrawing substituents:
    - Electron withdrawing substituents stabilize anions, so they increase neutral acidity and decrease anion basicity
    - Electron donating substituents will destabilize anions, so they decrease neutral acidity and increase anion basicity.

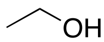
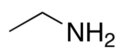
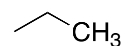
6. Ammonium Cations as Acids and Neutral Amines as Bases
    - Neutral amines are more basic than any neutral oxygen (electronegativity factor), and more basic than some resonance-stabilized oxygen anions.
    - Ammonium cations are more acidic than neutral nitrogen compounds or most neutral oxygen compounds, but less acidic than oxygens that give resonance-stabilized anions. (In this case, resonance factor trumps the charge factor).

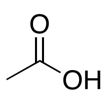
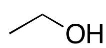
<u>Acid/Base Problems</u>

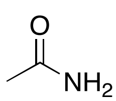
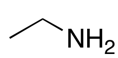
<u>Choose the More Acidic for Each of the Following Pairs: Single Variable Problems</u>

1. NH_3 $\oplus NH_4$

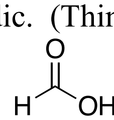
2.  

3.   

4.  

5.  

6. Rank the Acidity from 1 → 5, 1 being most acidic. (Think Anion! And Draw Anion!)

HF H_2O CH_3NH_2  CH_4

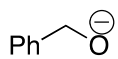
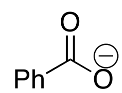
7. For the anions drawn in problem 6, rank them from 1 → 5 in terms of **<u>basicity</u>**.

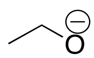
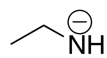
Choose the More **Basic** for Each of the Following Pairs (Single Variable)

1. NH_3 $NaNH_2$

2. NaOH H_2O

3. NH_3 H_2O

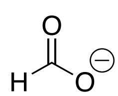
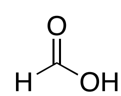
4.  

5.  

Predicting Acid/Base Equilibria: Any acid base equilibrium favors the side that has the more stable, less reactive base

6. Draw arrow to show whether equilibrium favors products or reactants. (Why?)

a. $H_2O + {}^{\ominus}NH_2$ $\quad$ ${}^{\ominus}OH + NH_3$

b. H_2O +  $\quad$ ${}^{\ominus}OH$ + 

Generic acid/base reaction, with anionic base and neutral acid:

$$HA + B^{\ominus} \rightleftharpoons A^{\ominus} + BH$$

Stronger acid → weaker conjugate base
Weaker acid → stronger conjugate base

- Acid-base reactions always favor formation of the weaker acid and weaker base
- The weaker acid and weaker base are always on the same side
- The more stable anion is the weaker base

THEREFORE:

- The equilibrium will always favor the WEAKER, MORE STABLE ANION
- **IF YOU CAN IDENTIFY WHICH ANION IS MORE STABLE, YOU CAN PREDICT THE DIRECTION THE REACTION WILL GO**.
- This logic can be used to predict whether an anion can successfully deprotonate a neutral species.

7. Can $H_3C^{\ominus}$ deprotonate H_2O?